# COORDINATION COMPOUNDS POSSESSING STANNYLAMINES: SYNTHESIS, CHARACTERIZATION, AND APPLICATION

A Thesis Presented to the Academic Faculty

by

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In Partial Fulfillment of the Requirements for the Degree
Doctor of Philosophy in Chemistry

Georgia Institute of Technology
August 2004

COORDINATION COMPOUNDS POSSESSING STANNYLAMINES: SYNTHESIS, CHARACTERIZATION, AND APPLICATION

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# DEDICATION

This work is dedicated to my wife, Angie Gray, my parents, Mr. and Mrs. David Eichler, my grandmother, Rita Eichler, and to the memory of my grandfather, Jack Eichler.

ACKNOWLEDGEMENT

I would like to first acknowledge Professor William S. Rees, Jr. for supporting my graduate career. In addition, I would like to acknowledge Dr. Oliver Just for performing all of the single crystal X-ray diffraction analyses reported in this dissertation and for providing both academic and personal counsel during my time at Georgia Tech. I would also like to thank Dr. Scott Bunge and Dr. Javier Concepcion for providing assistance in general laboratory matters and for providing useful insight regarding my research project, Professor Christoph Fahrni for lending his expertise in the interpretation of the photochemical measurements, Dr. Xi Zeng for performing SEM experiments, Qian Luo for completing all XPS measurements, David Bostwick for assisting in the mass spectrometry analyses, and Dr. Johannes Leissen and Dr. Leslie Gelbaum for their assistance in performing NMR experiments. Finally, I would like to send my gratitude to all of the members of my research group for their support and friendship. The work presented in this dissertation was financially supported by the Office of Naval Research and Molecular Design Institute, and for this I am truly grateful.

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LIST OF SYMBOLS AND ABBREVIATIONS

| | |
|---|---|
| Å | Angstrom |
| C | Celsius |
| d | doublet |
| EI | Electron Ionization |
| $Et_2O$ | diethyl ether |
| eV | electron volt |
| HOMO | Highest Occupied Molecular Orbital |
| IR | Infrared |
| K | Kelvin |
| λ | wavelength |
| LUMO | Lowest Unoccupied Molecular Orbital |
| m | multiplet |
| MHz | Megahertz |
| MOCVD | Metal Organic Chemical Vapor Depostion |
| MS | Mass Spectrometry |
| NMR | Nuclear Magnetic Resonance |
| ORTEP | Oak Ridge Thermal Ellipsoid Plot |
| ppm | parts per million |
| s | singlet |
| sccm | standard cubic centimeters per minute |
| SEM | Scanning Electron Microscopy |
| THF | tetrahydrofuran |

| | |
|---|---|
| TGA | Thermogravimetric Analysis |
| TMS | tetramethyl silane |
| UV/VIS | Ultraviolet/Visible |
| XPS | X-ray Photoelectron Spectroscopy |
| ZTT | Zirconium Tin Titanate |

# SUMMARY

The marriage of synthetic chemistry to materials science has been well documented in the last decade. The design, synthesis, and utilization of chemical precursors in the MOCVD of electronic materials in particular has received a lot of attention in both academic and industrial circles. The maintenance of this symbiotic relationship is pursued in this work in the hope of discovering chemical forerunners for high-dielectric metal oxide materials. Specifically, it is of interest to isolate chemical precursors for ZTT, a recent entry into the field of high-k dielectrics.

The primary theme of this dissertation is the exploration of the design and synthesis of molecular precursors that possess more than one of the cations found in the final ZTT film. The approach taken to obtain such precursors, referred to in this work as "same-source" precursors, is to investigate the implementation of the anionic stannylamine ligand, $^{-}N(SnMe_3)_2$ in the preparation of heterometallic coordination complexes. The ultimate goal is to procure volatile, low molecular weight compounds that possess more than one of the metals found in ZTT (tin, titanium, and/or zirconium).

The reason for choosing stannylamine ligands is two-fold. First, as was alluded to above, such ligands might provide convenient access to heterometallic complexes possessing tin as one of the metal constituents. Second, since the coordination chemistry of stannyl amines is relatively unexplored compared to alkyl- and silylamine ligands, it is important from a fundamental standpoint to investigate the synthetic utility of this ligand type.

Thus, this work accomplishes two major objectives: 1) the synthesis and characterization of a variety of metal complexes coordinated by stannylamines and 2) the design, synthesis, and utilization of heterometallic precursors for use in the MOCVD of ZTT. Chapter 1 summarizes the history of stannylamine coordination chemistry and the different binding modes possible in these types of ligands. Chapters 2-4 report the synthesis and complete characterization of lithiated stannylamines and their subsequent use in the preparation of beryllium, silver, zinc, and zirconium amides. Chapter 5 then describes the use of lithiated stannylamines as synthons to Group 14-nitrogen heterocubanes and the subsequent molecular design of tin-nitrogen cubanes for potential use in the MOCVD of ZTT. Finally, Chapter 6 provides details of the synthesis and characterization of a new class of heterometallic aminoalkoxides and their use in the MOCVD of ZTT.

To summarize, in the course of a synthetic investigation towards the goal of "same-source" ZTT precursors for use in MOCVD processes, a number of metal coordination complexes possessing stannylamine ligands have been synthesized and fully characterized. Consequently, the library of known compounds containing these ligands has been significantly expanded and a novel route to volatile, heterobimetallic aminoalkoxide species has been developed.

# CHAPTER 1

# INTRODUCTION

As the size requirements for integrated circuit devices become smaller, the utility of $SiO_2$ as the dielectric material in field effect transistors (FET's) will diminish.[1] This is due to the inherently high leakage current that arises when the thickness of the $SiO_2$ dielectric layer is decreased. Scaling of FET devices is governed by the duality of speed versus power. There is a desire to increase the speed of the device, which is dependent on drive current. Additionally, there is a need to decrease the power consumption, which is dependent on the gate leakage current.

$$(1)\ I \propto \mu C_{ox}$$

$$(2)\ C_{ox} \propto k/t$$

$$(3)\ I_g \propto 1/t$$

I = drive current

$\mu$ = effective mobility of carriers

$C_{ox}$ = gate oxide capacitance

$k$ = gate oxide dielectric constant

t = gate oxide thickness

$I_g$ = gate oxide leakage current

Since $SiO_2$ has a low dielectric constant ($k = 4$), higher capacitance, and hence larger drive currents are obtained by decreasing the thickness of the dielectric layer. However, decreasing the thickness of this layer leads to larger leakage currents, and thus increased power consumption. Current projections indicate that $SiO_2$ most likely will not meet device performance requirements due to scaling within the next decade.[2] A potential solution to this problem is to replace the silica dielectric layer with alternative metal

oxide materials possessing higher dielectric constants. Thicker dielectric layers can achieve the necessary capacitance if the material's dielectric constant is higher. Materials with larger dielectric constants thus have the potential to both decrease leakage currents (power consumption) and increase the drive current (transistor speed).

A number of oxide materials have been proposed as candidates to replace $SiO_2$ as the gate dielectric. Included among these are: $Ta_2O_5$, $TiO_2$, $Y_2O_3$, $CeO_2$, $ZrO_2$, $HfO_2$, $Al_2O_3$, and barium strontium titanate (BST). However, many of these materials are not easily integrated into the current device technology. A recent entry into this group of potential alternative dielectric materials is zirconium tin titanate (ZTT). High-*k* ZTT films were first deposited by van Dover and coworkers using an on-axis reactive sputtering technique. The electrical properties of these films were observed to be quite promising, possessing dielectric constants between 50-70 and leakage currents on the order of $10^{-9}$-$10^{-7}$ A/cm$^2$.[3] However, MOCVD processes offer distinct advantages relative to sputtering techniques, such as higher uniformity films, and are currently used in the deposition of numerous oxide films in the IC industry.

Hence, recent work by Senzaki, *et al*., as well as researchers in our group, has investigated the use of metal organic chemical vapor deposition (MOCVD) in the preparation of ZTT films. ZTT films were fabricated by both groups using a CVD precursor mixture comprised of $(^tBuO)_4M$ [M = Zr, Sn, Ti], but were found to posses dielectric constants between 20-30.[4,5] Since the dielectric constant of these films is significantly lower than in the films obtained by van Dover, *et al*., there is a need to optimize the MOCVD of ZTT. One aspect of the process that can be potentially improved is the nature of the chemical precususor system. Since the previously used

cocktail was a mixture of three individual chemical components, the use of a same-source precusor that contains two or more of the desired metal cations may prove to be a better alternative. Such a precursor system has the potential to limit premature reactions, provide good quality homogenous films, avoid varying decomposition regimes, and control the ratio of cations in the final film.[6-8]

Thus, the research presented in this dissertation focuses on designing and synthesizing same-source precursors that are to be used in the MOCVD of ZTT. The primary objective is to explore potential metal amide precursors and/or precursors that possess two or more of the metals of interest. The use of stannyl amide metal complexes may provide a route to such precursors.

The use of amido ligands (with amido generally refering to a deprotonated secondary amine; ¯NRR') in metal complexes is ubiquitous throughout the periodic table. Extensive research studies involving the synthesis, characterization, and application of metal amide compounds can be readily found in the literature and a number of publications devoted to reviewing the field of amidometal chemistry are available to the reader.[9-15] Interest in metal amide compounds arises, in part, from the potential for di-subsitution on the amide ligand. This allows the electronic and steric properties to be finely tuned, and metal coordination compounds of amides have found application in areas such as homogeneous catalysis,[16,17] organic synthesis,[18] small molecule activation,[19] and MOCVD of thin films.[6]

Due to the enhanced stability of the metal-nitrogen interaction that results from the steric protection of the bulky trimethyl silyl group and the electronic stabilization that potentially arises from the empty d-orbitals present on the silicon atoms, silyl amide

complexes [$M^{x+}(N(SiR_3)_2)_x$; R = alkyl, aryl] have been utilized in the preparation of a plethora of complexes.[13,20-22] Although metal amide compounds containing silyl substituents have been systematically studied, complexes possessing the heavier stannyl amide congener are much less frequent. Table 1.1 contains a list of structurally characterized metal complexes containing amide ligands with at least one trimethyl stannyl moiety.

**Table 1.1**. Metal complexes with $N(SnMe_3)_3$, $^{-}N(SnMe_3)(R)$, or $^{2-}N(SnMe_3)$ as a ligand

| Complex | Ref. | Complex | Ref. |
|---|---|---|---|
| $[Ti(Cl)\{O(2,6\text{-}(Ph)_2Ph)\}_2\{N(SnMe_3)_2\}]$ | 23 | $[Li\{O(CH_3)(^tBu)\}\{\mu\text{-}N(SnMe_3)_2\}]_2$ | 27 |
| $[In(CH_3)_2\{\mu\text{-}N(CH_3)(SnMe_3)\}]_2$ | 24 | $[Li\{\eta^3\text{-}N(CH_3)(CH_2CH_2NMe_2)_2)\}\text{-}\{N(SnMe_3)_2\}]_2$ | 27 |
| $[In(CH_3)_2\{\mu\text{-}N(^iPr)(SnMe_3)\}]_2$ | 24 | $[Ti(\eta^5\text{-}Cp)\{\mu_3\text{-}N(SnMe_3)\}]_4$ | 28 |
| $[Al(CH_3)_2\{\mu\text{-}N(^iPr)(SnMe_3)\}]_2$ | 24 | $[Li\{\eta^2\text{-}N(CH_3)_2CH_2CH_2N(CH_3)_2\}\text{-}\{\eta^2\text{-}N(Quinoline)(SnMe_3)\}]$ | 29 |
| $[Ga(CH_3)_2\{\mu\text{-}N(n\text{-}Propyl)(SnMe_3)\}]_2$ | 24 | $[Li\{\eta^3\text{-}N(CH_3)(CH_2CH_2N(CH_3)_2)_2\}\text{-}\{N(BC_8H_{14})(SnMe_3)\}]$ | 29 |
| $[Cu(Cl)\{N(SnMe_3)_3\}]$ | 25 | $[Ti(Cl)(\eta^5\text{-}Cp^*)\{\mu\text{-}N(SnMe_3)\}]_2$ | 30 |
| $[Cu\{\mu\text{-}N(SnMe_3)_2\}]_4$ | 25 | $[In(CH_3)_3\{N(SnMe_3)_3\}]$ | 31 |
| $[Al(Cl)_3\{N(SnMe_3)_3\}]$ | 26 | $[In(Cl)(CH_3)\{\mu\text{-}N(SnMe_3)_2\}]_2$ | 31 |
| $[Al(Cl)_2(CH_3)\{N(SnMe_3)_3\}]$ | 26 | $[In(Cl)(Et)\{\mu\text{-}N(SnMe_3)_2\}]_2$ | 31 |
| $[Ga(Cl)_3\{N(SnMe_3)_3\}]$ | 26 | $[Ti(F)\{\eta^5\text{-}Cp(Me_4)(Et)\}\{\mu\text{-}N(SnMe_3)\}]_2$ | 32 |
| $[Ga(Br)_3\{N(SnMe_3)_3\}]$ | 26 | $[Ga(CH_3)_2\{\mu\text{-}N(^iPr)(SnMe_3)\}]_2$ | 33 |
| $[Ga(Cl)_2(CH_3)\{N(SnMe_3)_3\}]$ | 26 | | |
| $[In(Cl)_3\{N(SnMe_3)_3\}]$ | 26 | | |
| $[In(Br)_3\{N(SnMe_3)_3\}]$ | 26 | | |

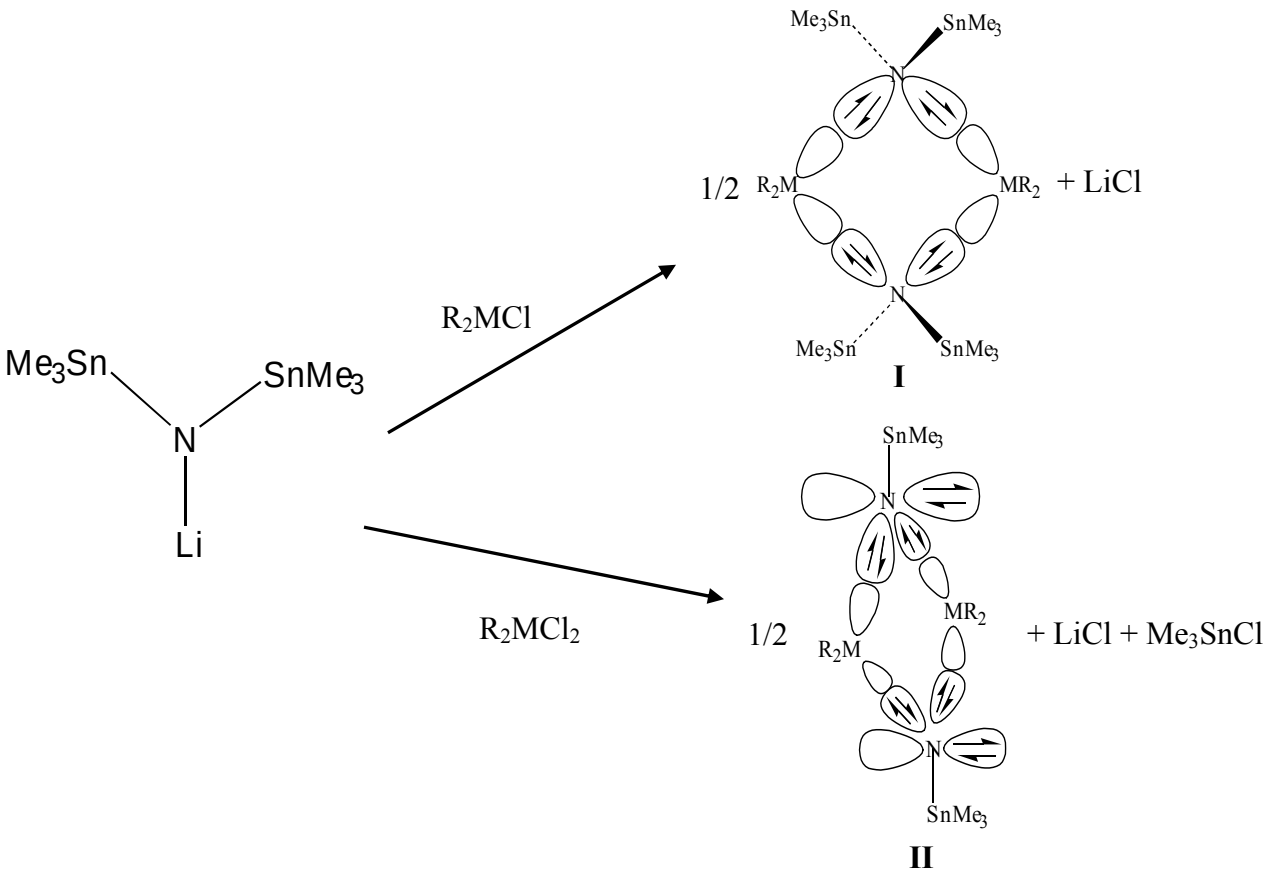
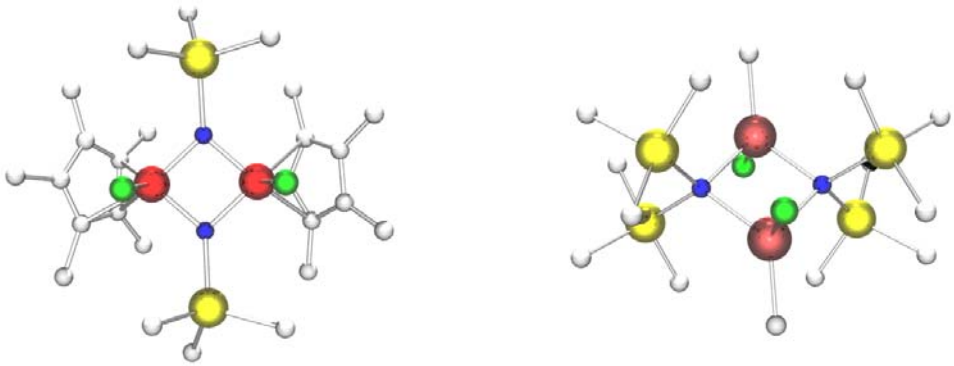



**Figure 1.1**. Bridging bonding mode of $^{-}N(SnMe_3)_2$ (**I**) and $^{2-}N(SnMe_3)$ (**II**)

The following chapters describe the use of either the monoanionic, $^{-}N(SnMe_3)_2$, or dianionic, $^{2-}N(SnMe_3)$, stannyl amides (as well as the silicon and germanium congeners) as ligands in metal complexes, with the ultimate aim of preparing heterometallic precursors for the MOCVD of ZTT. Examination of reported stannyl amide metal complexes possessing either mono or dianionic ligands reveals a tendency for these compounds to adopt dimeric or tetrameric structures (see Table 1.1). Figure 1.1 depicts valence bond representations of mono (**I**) and dianionic (**II**) forms of stannyl amide ligands. The ligand type **I** contains an $sp^3$ hybridized nitrogen, with two electron pairs coordinating to two metal centers in a bridging fashion. The ligand type **II** possesses an

$sp^2$ hybridized nitrogen, with two electron pairs residing in the $sp^2$ hybrid orbitals bridging two metal centers and another lone pair of electrons occupying an empty p orbital on the nitrogen atom. Figure 1.2 depicts crystal structures of metal complexes containing both monoanionic and dianionic stannyl amide ligands.



**A** **B**

**Figure 1.2**. Ball and stick rendering of $[Ti(Cl)(\eta^5\text{-}Cp^*)\{\mu\text{-}N(SnMe_3)\}]_2$[30] (**A**) and $[In(Cl)(CH_3)\{\mu\text{-}N(SnMe_3)_2\}]_2$[31] (**B**)

Sn N Ti In

Any design strategy involving the use of stannyl amido metal complexes must consider the potential to form either of these ligand types and their potential to undergo a bridging coordination mode.

The majority of the compounds listed in Table 1.1 were obtained by the reaction of the appropriate metal precursor with the tris(trimethylstannyl)amine $[(Me_3Sn)_3N]$ species. Conversely, Fenske and coworkers used the lithiated bis(trimethylstannyl)amine $[(Me_3Sn)_2NLi\bullet(THF)]$ in the preparation of the copper tetramer $[Cu\{\mu\text{-}N(SnMe_3)_2\}]_4$.[25] Based on computer database searches of the literature, this is the only stannyl amido metal complex synthesized via a lithium amide precursor. This complex should be

functional in a variety of metathesis reactions and could prove to be useful in the synthesis of ZTT MOCVD precursors. Thus, in an effort to expand the chemistry of this starting material, Chapter 2 explores the synthesis and full characterization of the lithiated bis(stannylamine) ligand. In addition, heteroleptic stannylamide ligands and beryllium complexes possessing stannylamide moities, synthesized using the lithium amide precursor reported by Fenske, are examined. These Group I and II complexes typically exist as dimers in the solid state, with the stannyl amide acting as a bridging ligand (Figure 1.3).

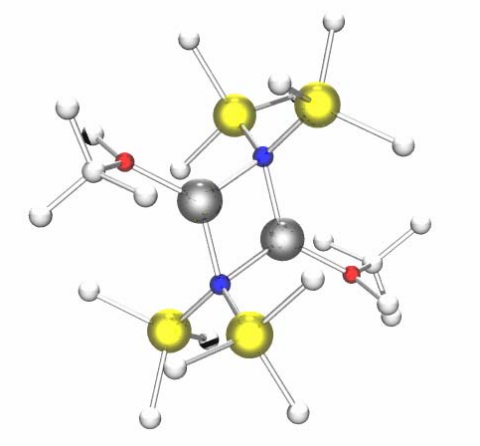


**Figure 1.3**. Ball and stick rendering of $[Li\{O(Me)(^tBu)\}\{\mu\text{-}N(SnMe_3)\}]_2$[27]

Sn ● N ● Li ● O ●

Before attempting to procure ZTT precursors, it was first of interest to determine the utility of $[(Me_3Sn)_2NLi\bullet(THF)]$ in metathesis reactions with various transition metal halide starting reagents. Thus, the reactivity of homoleptic and heteroleptic lithiated stannyl amides was first investigated with AgBr. The work in Chapter 3 aims to determine if silver tetrameric amido complexes structurally analogous to Fenske's copper tetramer, $[Cu\{\mu\text{-}N(SnMe_3)_2\}]_4$, can be synthesized. Lappert and coworkers first reported the synthesis of a silver amide possessing this planar $Ag_4N_4$ tetrameric core

approximately 8 years ago (Figure 1.4).[34] However, until recent work in our laboratory,[35] little has been done to investigate the possibility of extending this geometrical design to other ligand systems.

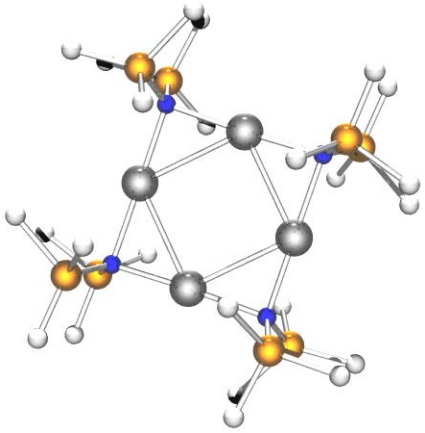


**Figure 1.4**. Ball and stick rendering of $[Ag\{\mu\text{-}N(SnMe_3)\}]_4$[34]

Si ● N ● Ag ●

The exploration of the chemistry of $[(Me_3Sn)_2NLi\bullet(THF)]$ with metal halide reagents is continued in Chapter 4, which describes reactions of N-lithio bis(trimethylstannyl)amine with zirconium and zinc chloride starting materials. The potential of stannyl amides to form either the monoanionic or dianionic ligand types previously described, and their subsequent complexes with zinc and zirconium are presented. The reaction pathways that are shown here are further explored in Chapter 5, resulting in the use of lithiated stannyl amides to prepare Group 14-nitrogen heterocubanes. Group 14 metal-nitrogen cubane structures have been previously obtained by a variety of alternative synthetic pathways, including the reaction of cyclic stannylenes with primary amines,[36] the reaction of magnesium imides with metal

dichlorides,[37] the reaction of lithiated primary amines with bis(cyclopentadienyl) metal complexes,[38] and the reaction of bis(amido) metal compounds with primary amines.[39] These structures exist as tetramers possessing an $M_4N_4$ core with an additional substituent bound to nitrogen in an exocube fashion (Figure 1.5). The work described here provides a novel, systematic route to a variety of cubane structures that possess unusually heavy exocube substituents, and the molecular design of these structures is probed in an attempt to fabricate ZTT MOCVD precursors.

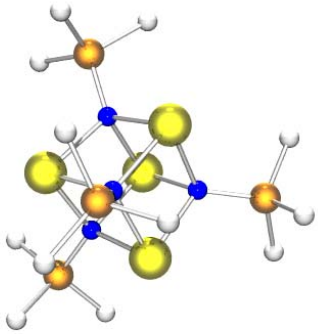


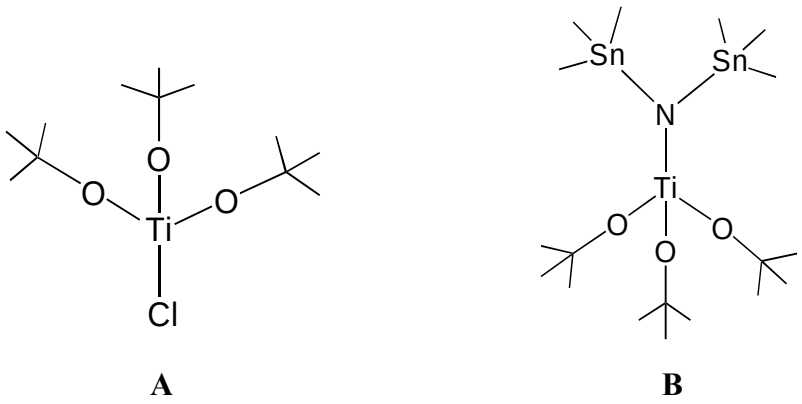
**Figure 1.5**. Ball and stick rendering of $[Sn\{\mu_3\text{-}N(SiMe_3)\}]_4$[36]

Sn ● N ● Si ●

Finally, in Chapters 6 and 7, both homoleptic and heteroleptic stannylamines are successfully implemented in the synthesis of same-source ZTT precursors. The resulting heterometallic stannyl amido metal complexes are then applied in the MOCVD of ZTT thin films. Chapter 6 describes the synthesis and characterization of tris(alkoxy)titanium chlorides, and their subsequent reaction with lithiated stannyl amines to produce heterometallic alkoxide-amides (Figure 1.6). A search of the literature indicates that bimetallic species containing nitrogen-bridged alkyl tin and titanium alkoxides have not

been previously reported. The investigation of the thermal properties of the tin-titanium alkoxide-amides and their use in the MOCVD of ZTT are then summarized in Chapter 7.

To conclude, during the course of a synthetic investigation related to the development of MOCVD precursors, a variety of stannyl amidometal complexes have been synthesized and characterized. Whether serendipitous or designed in nature, these complexes have further contributed to the development of the coordination chemistry of stannyl amide ligands, as well as provide potential alternative precursors in the MOCVD of ZTT.




**A** **B**

**Figure 1.6**. Diagram of tris(alkoxy)titanium chloride (**A**)[40] and heterometallic amido-alkoxide (**B**)

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# CHAPTER 2

# SYNTHESIS AND CHARACTERIZATION OF GROUP I AND II STANNYLAMIDES

## SECTION A: SYNTHESIS AND CHARACTERIZATION OF HOMOLEPTIC AND HETEROLEPTIC LITHIUM AMIDES POSSESSING THE TRIMETHYLSTANNYL MOIETY: $[(Me_3Sn)(Me_3E)NLi\bullet(Et_2O)]_2$ (E = Si, Ge, Sn)

### Introduction

Lithium dialkylamides and related N-lithiated species are an important class of organolithium reagents due to their extensive use in synthetic organic chemistry.[1] In addition, lithium amide species of this type provide convenient access to a wide range of metal amide compounds. Lithium amide species adopt numerous geometries in the solid state, including monomeric,[2] dimeric,[3] trimeric,[4] tetrameric,[5] and hexameric arrangements.[6] The structural characteristics of lithium amides and their use in the synthesis of amidometal compounds have been previously reviewed.[7,8]

Lithium bis(trimethylsilyl)amide and its derivatives have been used as amido transfer reagents in the preparation of a variety of metal amide complexes.[9] It was structurally characterized by Mootz and coworkers as a trimer,[4] and then later by Lappert, *et al*. as an ether-solvated dimer.[3] Although extensive research has been performed to understand the structural properties of lithiated silyl amines and their use as synthetic reagents in the preparation of metal amide compounds, little work has been put forth in the extension of this chemistry to the heavier *N*-lithiostannylamine congeners.

Fenske and coworkers first reported the synthesis of lithium bis(trimethylstannyl)amide and its subsequent utilization as a precursor of copper amide species.[10] However, little has been done since to structurally characterize this class of lithium amide complexes or explore their use in the synthesis of amidometal compounds. The lithiated stannylamines, $[\{(Me_3Sn)_2NLi(t\text{BuOMe})]_2$ and $[(Me_3Sn)_2NLi(pmdta)]$, (pmdta = *N*,*N*',*N*''-pentamethyldiethylenetriamine), reported by Wrackmeyer, *et al*. constitute the only examples of structurally characterized lithium stannylamides,[11] and these types of lithium amide precursors have not been utilized in the preparation of other amidometal species. Hence, it was desired to synthesize and characterize both homoleptic and heteroleptic lithiated stannylamines and further explore their use in the preparation of other metal amides.

The primary objective of this sub-chapter is to synthesize and isolate lithiated stannylamines as crystalline products. The need to accomplish this goal is two-fold: 1) precursors of this nature will ensure reagent purity and therefore minimize stoichiometric errors in subsequent reactions and 2) ease of manipulation and characterization. Thus, the synthesis and full characterization of the series of lithiated stannylamines, $[(Me_3Sn)_2NLi\bullet(THF)]_2$ (**1**), $[(Me_3Sn)(Me_3Si)NLi\bullet(Et_2O)]_2$ (**2**), and $[(Me_3Sn)(Me_3Ge)NLi\bullet(Et_2O)]_2$ (**3**) are reported herein.

**Experimental**

All manipulations were carried out in a dry atmosphere glovebox or by standard Schlenk techniques. All solvents were dried over Na° metal and were freshly distilled under an inert atmosphere prior to use. $Me_3GeCl$ was purchased from Gelest, and MeLi and

$Me_3SiCl$ were purchased from Aldrich and used without further purification. $(Me_3Sn)_3N$ was prepared according to literature procedures.[12] All NMR experiments were performed on a Bruker 400 MHz Spectrometer at 300K using $C_6D_6$ solvent that was distilled over $CaH_2$ and stored under argon. $^1H$, $^{13}C$, and $^{29}Si$ spectra were referenced to TMS. $^{119}Sn$ and $^7Li$ spectra were externally referenced to $Me_4Sn$ and LiBr respectively. Elemental analyses were performed in triplicate on a Perkin Elmer Series II CHNS/O Analyzer 2400.

*Synthesis of* $[(Me_3Sn)_2NLi\bullet(THF)]_2$ (**1**): A 12.4 mL sample of MeLi (1.6 M solution in hexane) was added dropwise at –30°C to a stirred solution of $(Me_3Sn)_3N$ (10.0g, 19.8 mmol) in diethyl ether (40 mL),. The reaction mixture was allowed to attain ambient temperature on its own and it was stirred overnight under an argon atmosphere. The resulting pale yellow solution was then reduced in volume, *in vacuo*, to about 30 mL, and from this colorless crystals were grown at –40°C over a two-day period. Yield: 4.62 g (56%); $^1H$ NMR (400 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ 0.31 (s, 36H, $CH_3$), 1.31 (m, 8H, $CH_2$), 3.62 (m, 8H, $CH_2$); $^{13}C$ NMR (100.6 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ 1.71 (s, $CH_3$), 25.22 (s, $CH_2$), 68.61 (s, $CH_2$); $^{119}Sn$ NMR (149.3 MHz, $C_6D_6$, 25ºC, $Me_4Sn$): $\delta$ 63.3 (s, $Sn(CH_3)_3$); $^7Li$ NMR (155.5 MHz, $C_6D_6$, 25ºC, LiBr): $\delta$ 1.69 (s); elemental analysis calculated (%) for $C_{20}H_{52}N_2O_2Li_2Sn_4$: C 28.55, H 6.23; found: C 27.86, H 6.24.

Crystal data for **1**. $C_{20}H_{52}N_2O_2Li_2Sn_4$: $M_r$ = 841.28 g cm$^{-3}$, crystal dimensions 0.46 x 0.27 x 0.24 mm, tetragonal, space group *P*-4*n*2, $a$ = 9.936(3), $c$ = 17.727(5) Å, $\beta$ = 90º; $V$ = 1750.0(8) Å$^3$, $Z$ = 2, $\rho_{calcd}$ = 1.597 g cm$^{-3}$, Siemens SMART CCD diffractometer, 2.35 ≤ $\theta$ ≤ 28.74˚,$Mo_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å), $\omega$ scans, $T$ = 193(2) K; of 4898 measured

reflections, 2,113 were independent and 1376 observed with $I > 2\sigma(I)$, $-3 \leq h \leq 13$, $-9 \leq k \leq 10$, $-23 \leq l \leq 23$; $R_1 = 0.0487$, $wR_2 = 0.1290$, GOF = 0.981 for 77 parameters, $\Delta\rho_{max} = 1.636$ eÅ$^{-3}$. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-97), Lorentz polarization corrections and absorption correction (SADABS) were applied, $\mu = 2.836$ mm$^{-1}$, min./max. transmission 0.5518/0.3560.

*Synthesis of [(Me$_3$Sn)(Me$_3$Si)NLi•(Et$_2$O)]$_2$* (**2**): $Me_3SiCl$ (1.12 g, 10.30 mmol) was added dropwise at 0°C to a stirred solution of $[(Me_3Sn)_2NLi•(THF)]_2$ (4.32 g, 5.15 mmol) in diethyl ether (40 mL). After the reaction mixture reached ambient temperature, a colorless precipitate formed within 10 minutes. The solution was stirred overnight under an argon atmosphere and then it was filtered through a Schlenk frit. The resulting clear, colorless solution was cooled to –30°C and, under vigorous stirring, MeLi (6.4 mL of 1.6 M solution in hexane) was added. The reaction mixture was allowed to reach room temperature on its own and it was subsequently stirred overnight under an argon atmosphere. The volume of solution was reduced, *in vacuo*, to about 30 mL and from this colorless crystals were grown at –40°C over a two-day period. Yield: 2.45 g (72%); $^1$H NMR (400 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ 0.22 (s, 18H, $SiMe_3$), 0.40 (s, 18H, $SnMe_3$), 1.29 (m, 8H, $CH_2$), 3.61 (m, 8H, $CH_2$); $^{13}$C NMR (100.6 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ -2.72 (s, $SiMe_3$), 7.16 (s, $SnMe_3$), 25.28 (s, $CH_2$), 68.47 (s, $CH_2$); $^{29}$Si NMR (79 MHz, $C_6D_6$, 25ºC, $Me_4Si$): $\delta$ -8.41 (s, $SiMe_3$); $^{119}$Sn NMR (149.3 MHz, $C_6D_6$, 25ºC, $Me_4Sn$): $\delta$ 34.4 (s, $SnMe_3$); $^7$Li NMR (155.5 MHz, $C_6D_6$, 25ºC, LiBr): $\delta$ 1.47 (s); elemental analysis calculated (%) for $C_{20}H_{52}N_2O_2Li_2Si_2Sn_2$: C 36.39, H 7.94; found: C 38.44, H 8.30.

Crystal data for **2**. $C_{20}H_{56}N_2O_2Li_2Si_2Sn_2$: $M_r$ = 664.11 g cm$^{-3}$, crystal dimensions 0.37 x 0.27 x 0.17 mm, tetragonal, space group *P*-4*n*2, $a$ = 9.788(3), $c$ = 17.406(9) Å, $\beta$ = 90º; $V$ = 1667.7(11) Å$^3$, $Z$ = 2, $\rho_{calcd}$ = 1.323 g cm$^{-3}$, Siemens SMART CCD diffractometer, 2.34 ≤ $\theta$ ≤ 28.71˚,$Mo_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å), $\omega$ scans, $T$ = 193(2) K; of 9,799 measured reflections, 2,074 were independent and 1,739 observed with $I > 2\sigma(I)$, -13 ≤ $h$ ≤ 13, -12 ≤ $k$ ≤ 10, -23 ≤ $l$ ≤ 15; $R_1$ = 0.0434, $wR_2$ = 0.0953, GOF = 1.061 for 79 parameters, $\Delta\rho_{max}$ = 0.552 eÅ$^{-3}$. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-97), Lorentz polarization corrections and absorption correction (SADABS) were applied, $\mu$ = 1.585 mm$^{-1}$, min./max. transmission 0.7744/0.5887.

*Synthesis of [(Me$_3$Sn)(Me$_3$Ge)NLi•(Et$_2$O)]$_2$* (**3**): Compound **3** was prepared using [(Me$_3$Sn)$_2$NLi•(THF)]$_2$ (4.55 g, 5.40 mmol), Me$_3$GeCl (1.65 g, 10.80 mmol), and MeLi (6.75 mL of a 1.6 M solution in hexane) in an analogous manner to compound **2**. Colorless crystals were grown from diethyl ether at –40°C over a two-day period. Yield: 2.22 g (55%); $^1$H NMR (400 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ 0.23 (s, 18H; $CH_3Sn$), 0.42 (s, 18H; $CH_3Ge$), 1.03 (t, 12H; $CH_3$), 3.39 (q, 8H; $CH_2$); $^{13}$C NMR (100.6 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ –1.52 (s, $CH_3Sn$), 6.96 (s, $CH_3Ge$), 14.85 (s, $CH_3$), 64.64 (s, $CH_2$); $^{119}$Sn NMR (149.3 MHz, $C_6D_6$, 25ºC, $Me_4Sn$): $\delta$ 46.73 (s, $Me_3Sn$); $^7$Li NMR (155.5 MHz, $C_6D_6$, 25ºC, LiBr): $\delta$ 1.66 (s); elemental analysis calculated (%) for $C_{20}H_{56}N_2O_2Li_2Ge_2Sn_2$: C 31.89, H 7.49, N 3.72; found: C 32.16, H 7.11, N 4.73.

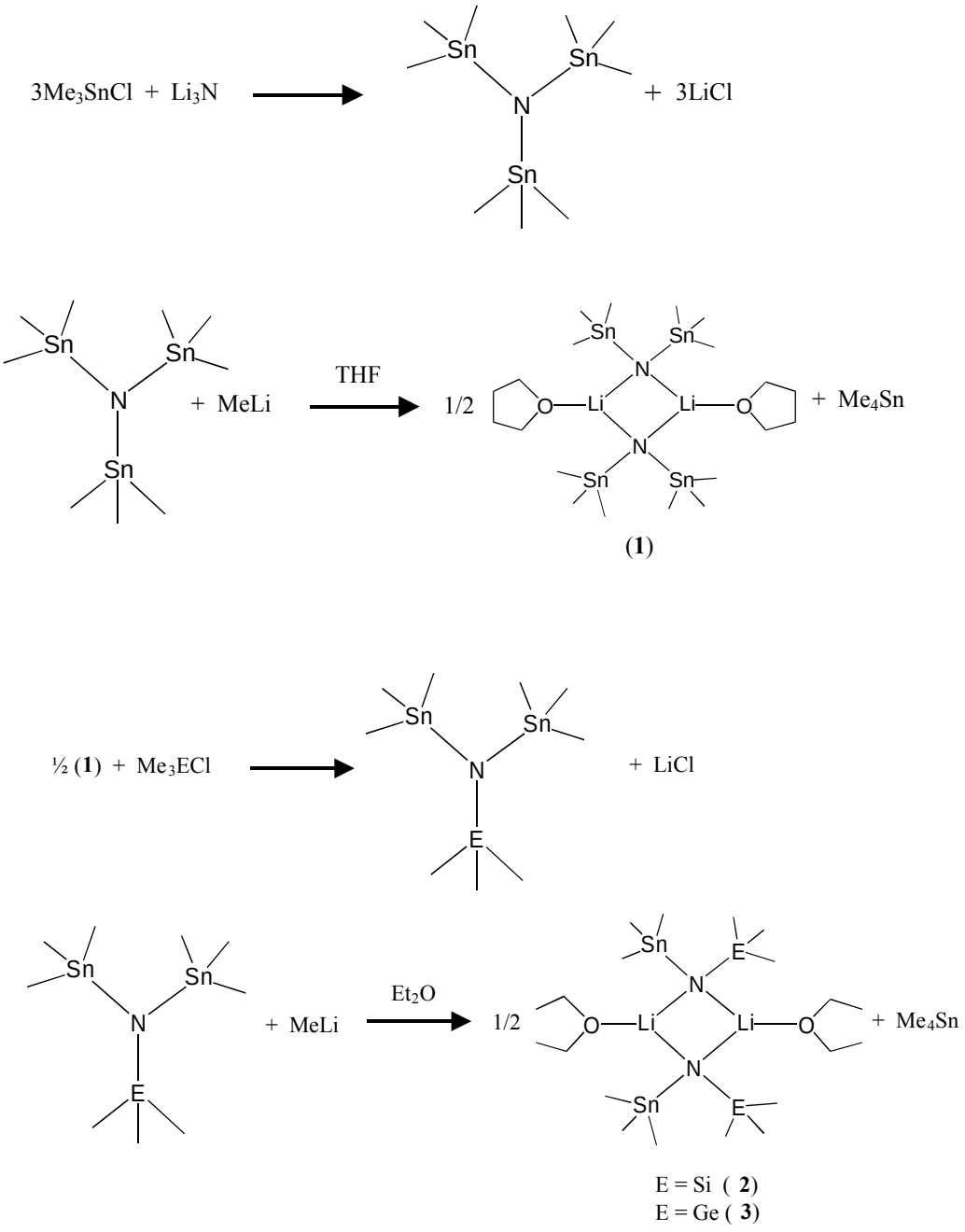
Crystal data for **3**: $C_{20}H_{56}N_2O_2Li_2Ge_2Sn_2$, $M_r$ = 753.11 g cm$^{-3}$, crystal dimensions 0.32 x 0.27 x 0.19 mm, tetragonal, space group *P*-4*n*2, $a$ = 9.7798(6), $c$ = 17.664(2) Å, $\beta$ = 90º;

$V$ = 1689.4(3) Å$^3$, $Z$ = 2, $\rho_{calcd}$ = 1.480 g cm$^{-3}$, Siemens SMART CCD diffractometer, 2.31 ≤ $\theta$ ≤ 28.73˚,Mo$_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å), $\omega$ scans, $T$ = 193(2) K; of 9,503 measured reflections, 2,087 were independent and 1,828 observed with $I > 2\sigma(I)$, -12 ≤ $h$ ≤ 12, -13 ≤ $k$ ≤ 11, -23 ≤ $l$ ≤ 11; $R_1$ = 0.0385, $wR_2$ = 0.0977, GOF = 1.075 for 80 parameters, $\Delta\rho_{max}$ = 0.616 eÅ$^{-3}$. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-97), Lorentz polarization corrections and absorption correction (SADABS) were applied, $\mu$ = 3.238 mm$^{-1}$, min./max. transmission 0.5827/0.4211.

**Results and Discussion**

*Synthesis*

The synthesis of compounds **1-3** is depicted in Scheme 2.1. Compound **1** was synthesized by a modification of the method originally reported by Fenske.[10] In the first step, three equivalents of trimethyltin chloride were reacted with lithium nitride to generate tris(trimethylstannyl)amine, which was then isolated by a vacuum distillation and reacted subsequently with an equivalent amount of methyl lithium. Upon completion of the reaction, compound **1** was recrystallized from THF at –40˚C, yielding colorless crystals. Crystals of **1**, found to be dimeric in the solid state, were dissolved in diethyl ether and reacted with two equivalents of $Me_3ECl$ (E = Si, Ge). After stirring overnight and filtering off the LiCl precipitate, two equivalents of MeLi were added *in situ*. The reaction was stirred overnight to produce compounds **2** and **3**, which were recrystallized from diethyl ether at –40˚C and isolated as colorless crystals in moderate yields.




**Scheme 2.1**. Synthesis of compounds **1-3.**

*Characterization*

Crystals of compounds **1-3** were each analyzed by a single crystal X-ray diffraction experiment. The results are shown in Figures 2.1-2.3.

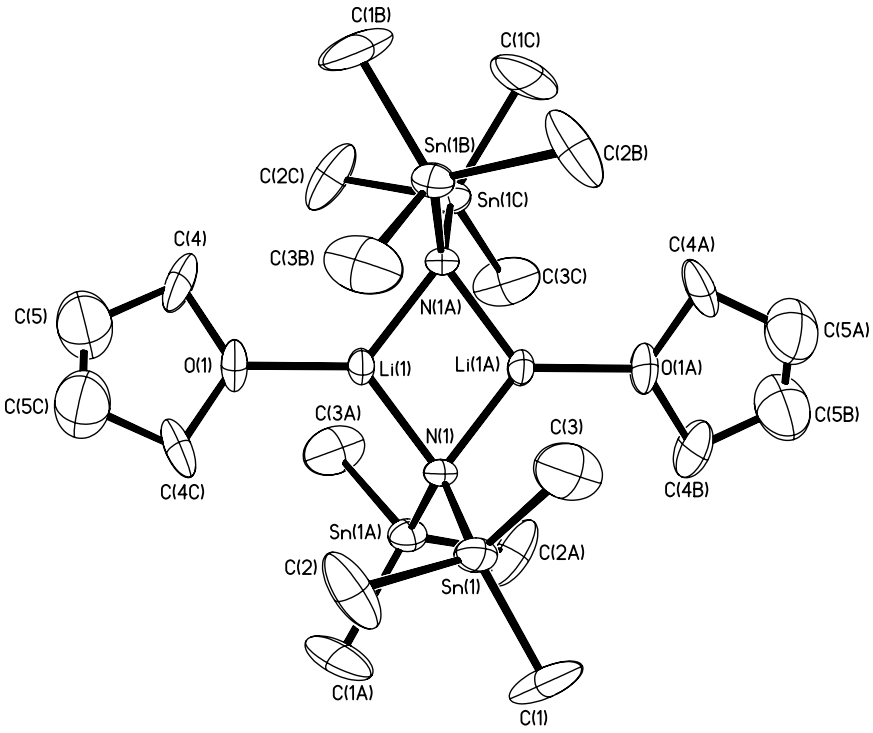



**Figure 2.1**. ORTEP plot representation (30% probability) with numbering scheme for compound **1**. Hydrogen atoms have been omitted for clarity.

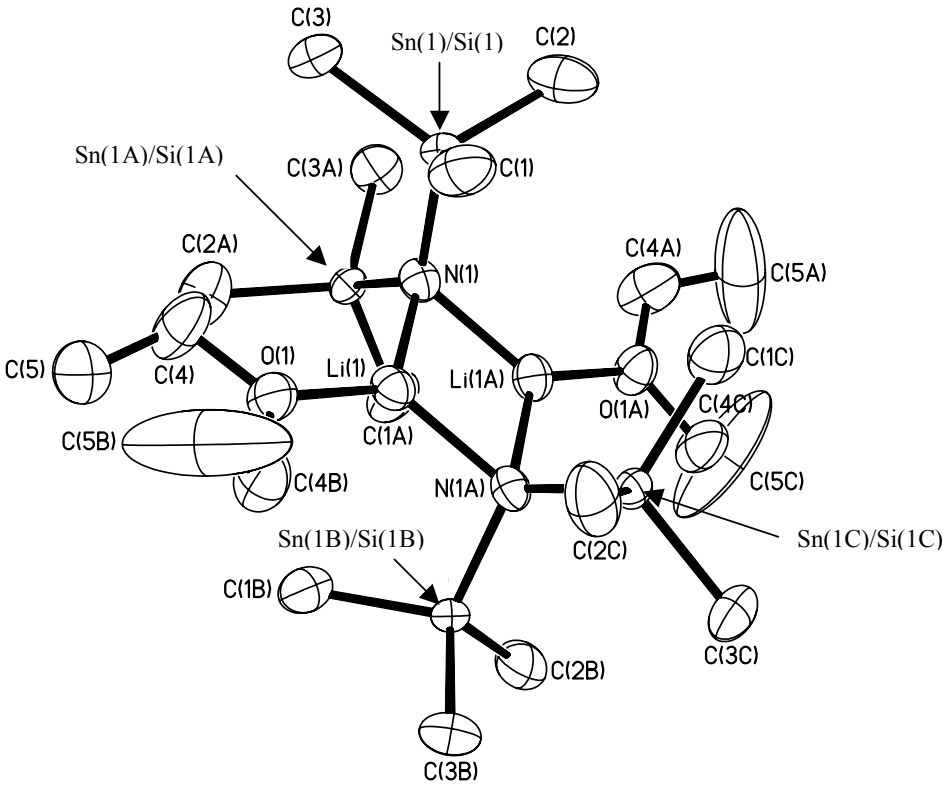



**Figure 2.2**. ORTEP plot representation (30% probability) with numbering scheme for compound **2**. Hydrogen atoms have been omitted for clarity.

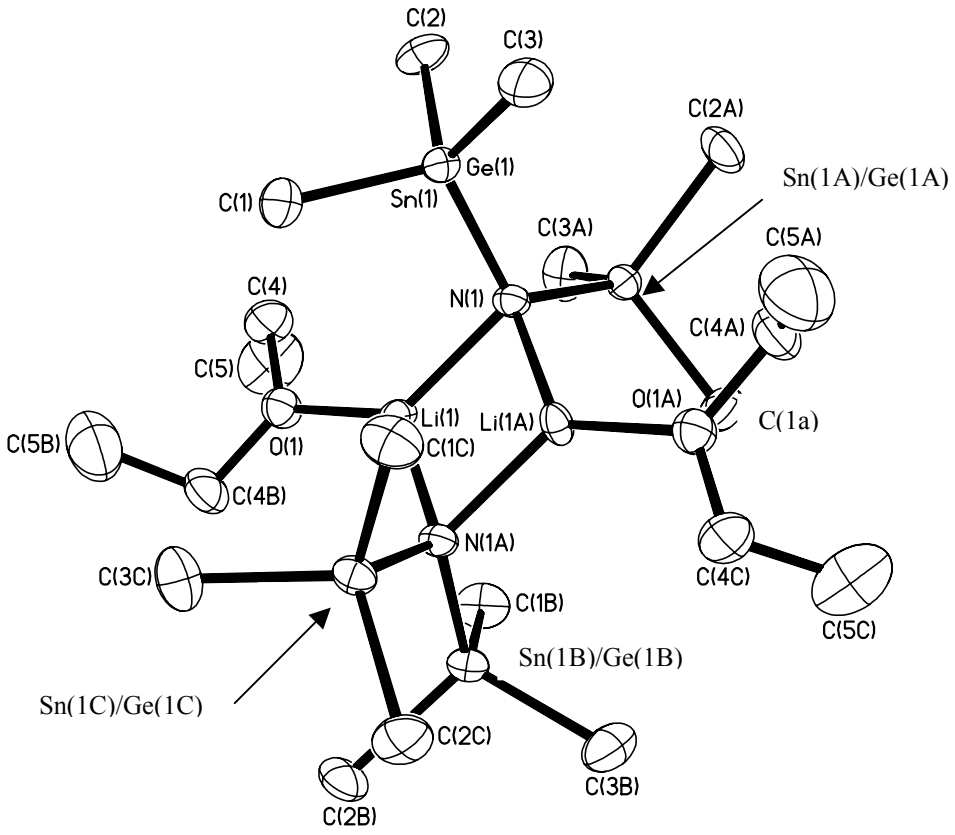



**Figure 2.3**. ORTEP plot representation (30% probability) with numbering scheme for compound **3**. Hydrogen atoms have been omitted for clarity.

All three complexes exist as lithium dimers in the solid state, with the bis(trimethylstannyl)amide acting as a bridging ligand, and THF or diethyl ether molecules terminally binding to the lithium metal centers. A summary of the principal interatomic distances and angles for compounds **1-3** is provided in Table 2.1, and a complete list of all distances and angles can be found in Tables A.2, A.6, and A.10, respectively.

**Table 2.1**. Selected average interatomic distances (Å) and angles (degrees) for compounds **1-3.**

| (**1**) | distance/angle | (**2**) | distance/angle | (**3**) | distance/angle |
|---|---|---|---|---|---|
| Sn-N | 2.022(4) | Sn/Si-N | 1.919(3) | Sn/Ge-N | 1.915(3) |
| Li-N | 1.935(14) | Li-N | 1.987(9) | Li-N | 1.980(8) |
| Li-O | 1.90(2) | Li-O | 1.921(14) | Li-O | 1.937(12) |
| Li-N-Li | 74.1(10) | Li-N-Li | 75.0(6) | Li-N-Li | 75.3(5) |
| N-Li-N | 105.9(10) | N-Li-N | 105.0(6) | N-Li-N | 104.7(5) |

Compounds **1-3** possess a $Li_2N_2$ rhombic core with the Li-N-Li and N-Li-N angles approximating 75˚ and 105˚, respectively. The Li-N and Li-O interatomic distances are in agreement with previously reported lithium amide dimers with terminally coordinated etherate molecules {$[(Me_3Sn)_2NLi•O(Me)(^tBu)]_2$, Li-N = 2.0115 Å and Li-O = 1.987 Å; $[(Me_3Si)_2NLi•OEt_2]_2$, Li-N = 2.06 Å and Li-O = 1.96 Å}.[3,11] As seen in Table 2.1, a trend of decreasing Li-N interatomic distance can be observed with the second amide substituent being a heavier Group 14 analogue. It suggests increased electron density

localized on the nitrogen atom with two heavier Group 14 elements attached. The tin-nitrogen interatomic distances also fall in the range observed for similar compounds {$[(Me_3Sn)_2NLi\cdot(^tBuMeO)]_2$, $Sn\text{-}N_{avg}$ = 2.093 Å}.[11] For compounds **2** and **3**, the Sn, Si, and Ge atoms were crystallographically indistinguishable. The observed interatomic distances were 1.919 Å for all Sn-N and Si-N interactions, and 1.915 Å for all Sn-N and Ge-N interactions. These values lie between the corresponding interatomic distances registered in the structurally analogous compounds: $[(Me_3Sn)_2NLi\cdot(^tBuMeO)]_2$, $Sn\text{-}N_{avg}$ = 2.093 Å and $[(Me_3Si)_2NLi\cdot Et_2O]_2$, $Si\text{-}N_{avg}$ = 1.705 Å;[3] $[(Me_3Sn)_2NLi\cdot(^tBuMeO)]_2$, $Sn\text{-}N_{avg}$ = 2.093 Å[11] and $[LiN(GeMe_3)_2]_3$, $Ge\text{-}N_{avg}$ = 1.837 Å.[13] The presence of germanium and silicon in the heteroleptic compounds **2** and **3** was confirmed by the $^{119}Sn$ NMR chemical shifts for the two compounds (Figure 2.4) and the elemental analyses.

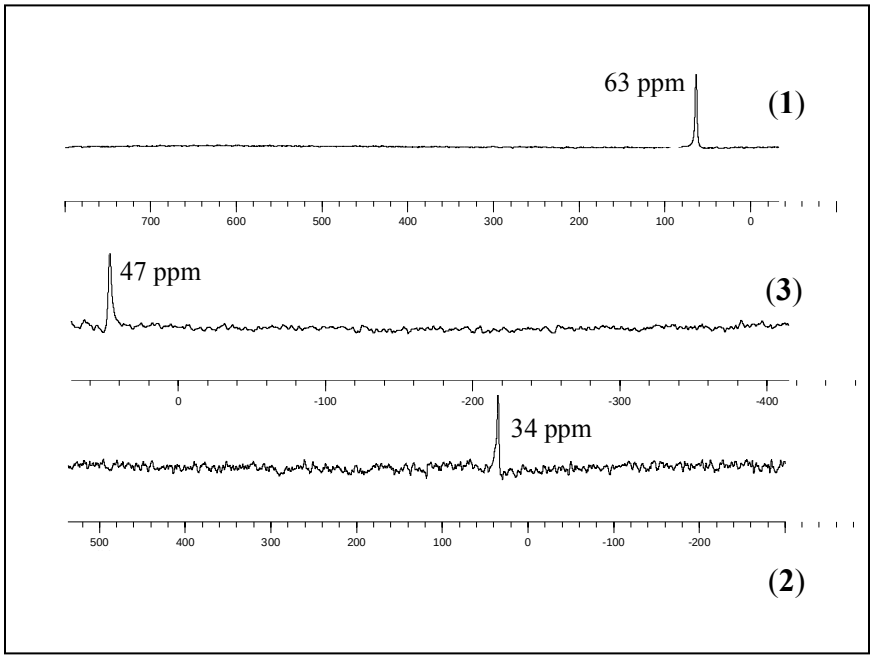



**Figure 2.4**. $^{119}Sn$ NMR spectra of compounds **1-3** (chemical shift scale in ppm).

## Conclusion

In summary, compound **1** was prepared using a modified version of Fenske's synthesis and used as a precursor to obtain the heteroleptic lithiated stannylamines, **2** and **3**. All three complexes were isolated as analytically pure, colorless crystals. Compounds **1-3** were structurally characterized by a single crystal X-ray diffraction study, and the molecular structures were verified by multinuclear NMR and elemental analyses. These species add to the limited library of lithiated stannylamines and will be subsequently used as synthons to other metal amide compounds.

## SECTION B: SYNTHESIS AND CHARACTERIZATION OF BERYLLIUM AMIDES PREPARED VIA LITHIATED STANNYLAMINES: $[(Me_3Sn)_2NBe(Cl)\bullet(THF)]_2$ AND $[(Me_3Si)(H)NBe(Cl)\bullet(THF)]_2$

### Introduction

Due to the high toxicity of its compounds, the chemistry of beryllium remains relatively unexplored compared to that of its neighboring elements. A majority of the structurally characterized beryllium amido complexes carry either dialkyl or silyl amide ligands. A comprehensive review of beryllium amide chemistry has been compiled by Lappert and coworkers.[9]

A literature search revealed that beryllium amide compounds possessing stannyl amide ligands have not, to date, been reported. Previous studies show that amido beryllium species can be prepared via the reaction of lithiated amines and $BeCl_2$.[14] Thus, the lithiated stannyl amines previously described in Chapter 2 – Part A have the potential to provide an avenue to a new class of beryllium amides. This sub-chapter explores the reaction of compounds **1**-**3** with $BeCl_2$, leading to the synthesis and characterization of the dimeric beryllium amides, $[(Me_3Sn)_2NBe(Cl)\bullet(THF)]_2$ (**4**) and $[(Me_3Si)(H)NBe(Cl)\bullet(THF)]_2$ (**5**). Additionally, compound **4** was employed as a synthon in the preparation of $[(Me_3Sn)_2NBe(OSO_2CF_3)]_2$ (**6**).

### Experimental

All manipulations were carried out in a dry atmosphere glovebox or by standard Schlenk techniques. All solvents were dried over Na° metal and were freshly distilled under an

inert atmosphere prior to use. $BeCl_2$ was purchased from Alfa Aesar and compounds (**1**) and (**2**) were prepared as described in Chapter 2 – Part A. All solution state NMR experiments were performed on a Bruker 400 MHz Spectrometer at 300 K using $C_6D_6$ solvent that was distilled over $CaH_2$ and stored under argon. $^{1}H$ and $^{13}C$ spectra were referenced to TMS. $^{119}Sn$ and $^{9}Be$ spectra were externally referenced to $Me_4Sn$ and $BeSO_4$, respectively. All solid state NMR experiments were performed on a Bruker DSX 400 MHz spectrometer and all samples were analysed using a 4 mm MAS rotor. $^{9}Be$ spectra were externally referenced to an aqueous solution of $BeSO_4$. Elemental analyses were performed in triplicate on a Perkin Elmer Series II CHNS/O Analyzer 2400, FT-IR measurements were performed on a Bruker Equinox 55 Spectrometer, and mass spectrometry analyses were done on a VG Instruments 70SE (Electron Impact ionization; 70eV).

*Synthesis of* $[(Me_3Sn)_2NBe(Cl)\bullet(THF)]_2$ (**4**): A solution of $[(Me_3Sn)_2NLi\bullet(THF)]_2$ (1.00 g, 1.19 mmol) in diethyl ether (40 mL) was added dropwise to a diethyl ether slurry of $BeCl_2$ (0.19 g, 2.38 mmol) at 0°C. The reaction mixture was allowed to attain ambient temperature on its own, whereby a colorless precipitate formed within 10 minutes. After stirring overnight under an argon atmosphere the reaction mixture was filtered and its volume was reduced, *in vacuo*, to about 30 mL. Colorless crystals were grown from this solution at –40°C over a two-day period. Yield: 0.42 g (38%); $^{1}H$ NMR (400 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ 0.40 (s, 36H, $SnMe_3$), 1.39 (m, 8H, $CH_2$), 3.58 (m, 8H, $CH_2$); $^{13}C$ NMR (100.6 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ –1.89 (s, $SnMe_3$), 25.66 (s, $CH_2$), 68.55 (s, $CH_2$); $^{119}Sn$ NMR (149.3 MHz, $C_6D_6$, 25ºC, $Me_4Sn$): $\delta$ 75.1 (s, $SnMe_3$); $^{9}Be$ NMR (56

MHz, $CDCl_3$, 25ºC, $BeSO_4$): $\delta$ 13.71 (s); $^9$Be Solid State NMR (56 MHz, 25ºC, $BeSO_4$): $\delta$ 0.3 (s); MS (EI, 245°C): *m/z* 757 [$(M-15)^+$]; elemental analysis calculated (%) for $C_{20}H_{52}N_2O_2Cl_2Be_2Sn_4$: C 26.21, H 5.72; found: C 26.75, H 5.12.

Crystal data for **4**. $C_{20}H_{52}N_2O_2Cl_2Be_2Sn_4$: $M_r$ = 458.16 g cm$^{-3}$, crystal dimensions 0.27 x 0.20 x 0.12 mm, monoclinic, space group *P*2(1)/n, $a$ = 11.299(2), $b$ = 13.064(3), $c$ = 11.512(2) Å, α = 90, $\beta$ = 107.620(3)º; $V$ = 1619.7(5) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 1.879 g cm$^{-3}$, Siemens SMART CCD diffractometer, $2.21 \leq \theta \leq 28.88^\circ$, $Mo_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å), $\omega$ scans, $T$ = 193(2) K; of 10,272 measured reflections, 3909 were independent and 3,283 observed with $I > 2\sigma(I)$, $-14 \leq h \leq 13$, $-17 \leq k \leq 9$, $-14 \leq l \leq 15$; $R_1$ = 0.0585, $wR_2$ = 0.1516, GOF = 1.126 for 161 parameters, $\Delta\rho_{max}$ = 2.085 eÅ$^{-3}$. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-97), Lorentz polarization corrections and absorption correction (SADABS) were applied, $\mu$ = 3.232 mm$^{-1}$, min./max. transmission 0.6997/0.4735.

*Synthesis of [(Me$_3$Si)(H)NBe(Cl)•(THF)]$_2$* (**5**): Compound **5** was prepared in an analogous fashion to compound **4** using [$(Me_3Sn)(Me_3Si)NLi•(Et_2O)]_2$ (1.00 g, 1.50 mmol) and $BeCl_2$ (0.24 g, 3.00 mmol). Colorless crystals were grown at –40°C over a two-day period. Yield: 0.22 g (36%); IR (nujol): 3270 (w), 1261 (m), 1905 (s), 807 (s), 667 (w), 599 (w) cm$^{-1}$.

Crystal data for **5**. $C_{14}H_{36}N_2O_2Cl_2Be_2Si_2$: $M_r$ = 409.55 g cm$^{-3}$, crystal dimensions 0.136 x 0.119 x 0.102 mm, tetragonal, space group *P*4(3)2(1)2, $a$ = 11.3551(12), $c$ = 18.865(4) Å, $\beta$ = 90º; $V$ = 2432.4(6) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 1.118 g cm$^{-3}$, Siemens SMART CCD diffractometer, $2.09 \leq \theta \leq 25.05^\circ$, $Mo_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å), $\omega$ scans, $T$ = 193(2) K;

of 12,348 measured reflections, 2,165 were independent and 1,827 observed with $I > 2\sigma(I)$, $-13 \leq h \leq 13$, $-13 \leq k \leq 13$, $-22 \leq l \leq 16$; $R_1 = 0.0549$, $wR_2 = 0.1332$, GOF = 1.065 for 120 parameters, $\Delta\rho_{max} = 0.621$ eÅ$^{-3}$. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-97), Lorentz polarization corrections and absorption correction (SADABS) were applied, $\mu = 0.374$ mm$^{-1}$, min./max. transmission 0.9629/0.9510.

*Synthesis of [(Me$_3$Sn)$_2$NBe(OSO$_2$CF$_3$)]$_2$* (**6**): Compound **6** was prepared by stirring a mixture of 1.0 equivalents of **4** (0.65 g, 0.71 mmol) with 2.0 equivalents of Ag(OSO$_2$CF$_3$) (0.36 g, 1.42 mmol) in diethyl ether at –30ºC. The reaction mixture was allowed to attain ambient temperture on its own, stirred for 1.5 hours, and then filtered to remove all of the resulting precipitate. Colorless crystals were grown from this solution overnight at –10ºC. Yield: 0.22 g (31%); MS (EI, 245°C): *m/z* 985 [(M-15)$^+$]; IR (nujol): 3270 (w), 1261 (m), 1905 (s), 807 (s), 667 (w), 599 (w) cm$^{-1}$.

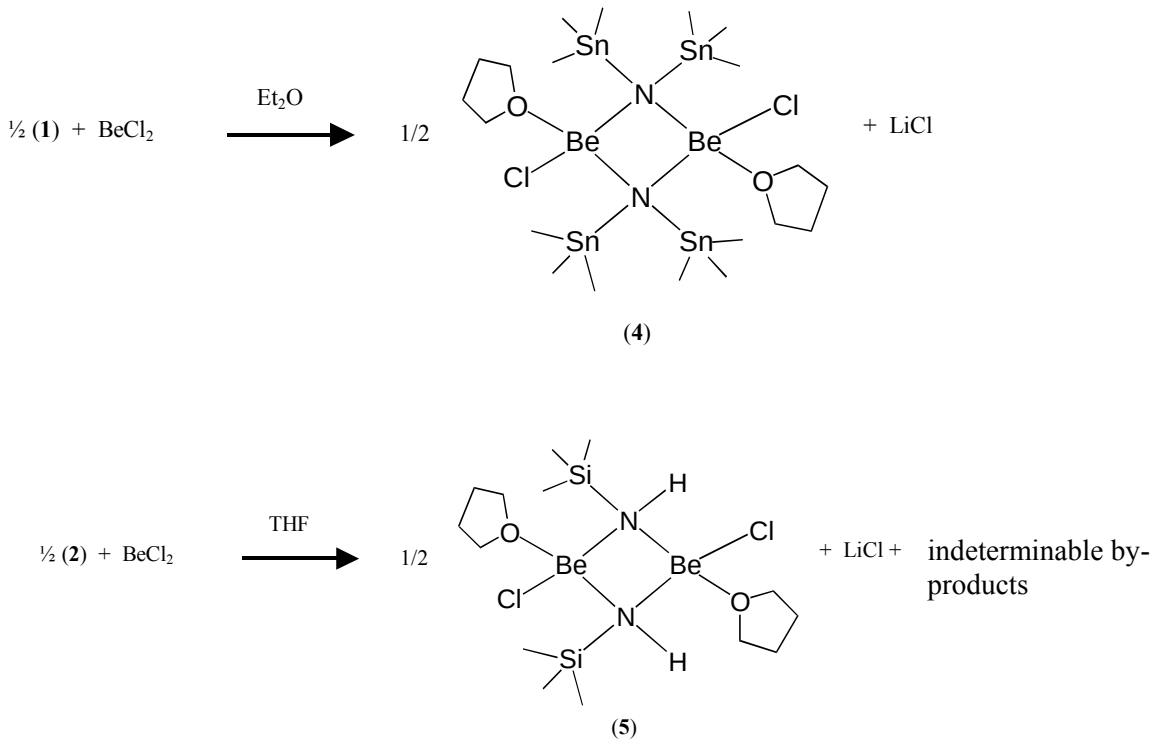
Crystal data for **6**. $C_{14}H_{36}N_2O_6S_2F_6Be_2Sn_4$: $M_r = 999.35$ g cm$^{-3}$, crystal dimensions 0.46 x 0.20 x 0.20 mm, monoclinic, space group $P2(1)/c$, $a = 19.203(3)$, $b = 10.5666(17)$, $c = 18.032(3)$ Å, $\alpha = 90º$, $\beta = 116.219º$; $V = 3282.4(9)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 2.022$ g cm$^{-3}$, Siemens SMART CCD diffractometer, $1.18 \leq \theta \leq 28.68º$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\omega$ scans, $T = 193(2)$ K; of 20,193 measured reflections, 7,724 were independent and 6,197 observed with $I > 2\sigma(I)$, $-21 \leq h \leq 25$, $-13 \leq k \leq 13$, $-23 \leq l \leq 17$; $R_1 = 0.0366$, $wR_2 = 0.0907$, GOF = 1.059 for 349 parameters, $\Delta\rho_{max} = 3.899$ eÅ$^{-3}$. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures

(SHELXL-97), Lorentz polarization corrections and absorption correction (SADABS) were applied, $\mu$ = 0.3.197 $mm^{-1}$, min./max. transmission 0.5616/0.3216.

## Results and Discussion

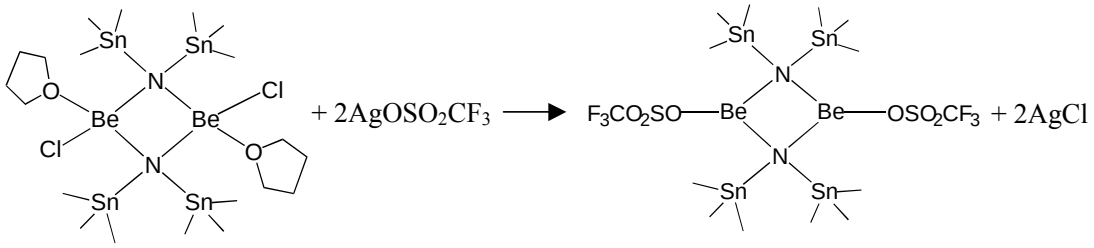
*Synthesis*

The synthesis of compounds **4** and **5**, shown in Scheme 2.2, was accomplished by reacting 2 equivalents of $BeCl_2$ with compounds **1** and **2**, respectively. After stirring overnight, the LiCl precipitate was filtered off and the products were recrystallized directly from the reaction solvent. Compound **4** was isolated in accordance with the expected reaction sequence, however, compound **5** was unexpectedly obtained (Scheme 2.2). Whether this complex formed due to the presence of moisture or because of an unanticipated reaction pathway is yet to be determined, as the reaction by-products could not be successfully characterized. The reaction of compound **3** with $BeCl_2$ led to indeterminable product mixtures.




**Scheme 2.2**. Synthesis of compounds **4-5.**

The synthesis of compound **6**, depicted in Scheme 2.3, was carried out via the reaction of compound **4** with two equivalents of silver(I)triflate. After stirring for one and a half hours at room temperature, the reaction mixture was filtered to remove the AgCl precipitate. The resulting beryllium dimer was recrystallized from diethyl ether at –10ºC.




**Scheme 2.3**. Synthesis of compound (**6**).

*Characterization*

Crystals of compounds **4-6** were analyzed by single crystal X-ray diffraction and the crystal structures of these compounds are given in Figures 2.5-2.7.

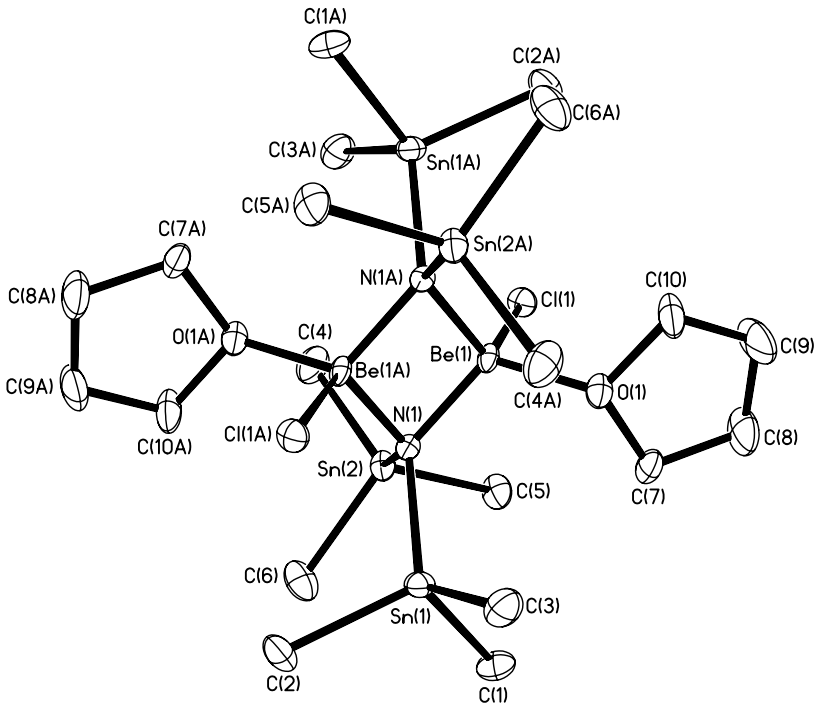



**Figure 2.5**. ORTEP plot representation (30% probability) with numbering scheme for compound **4**. Hydrogen atoms have been omitted for clarity.

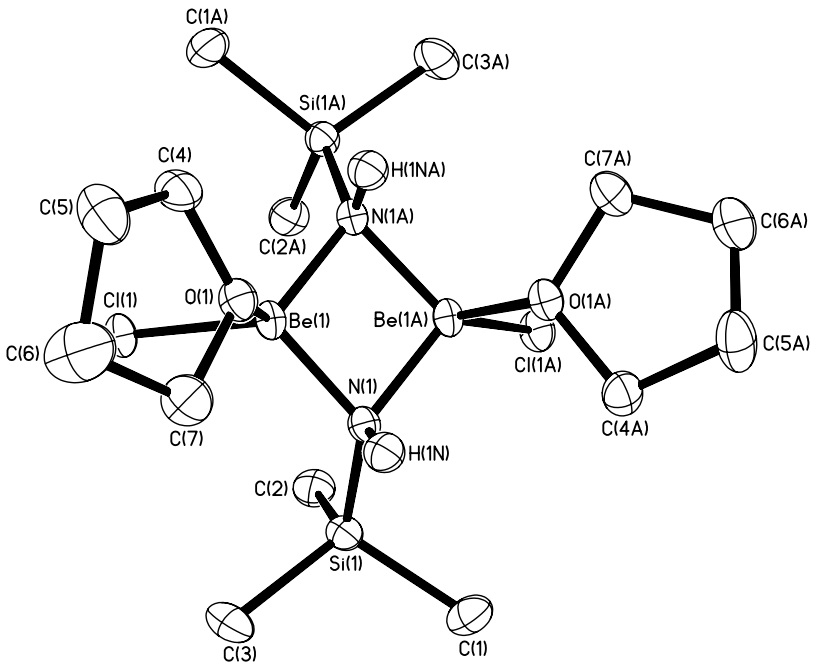



**Figure 2.6**. ORTEP plot representation (30% probability) with numbering scheme for compound **5**. Hydrogen atoms have been omitted for clarity.

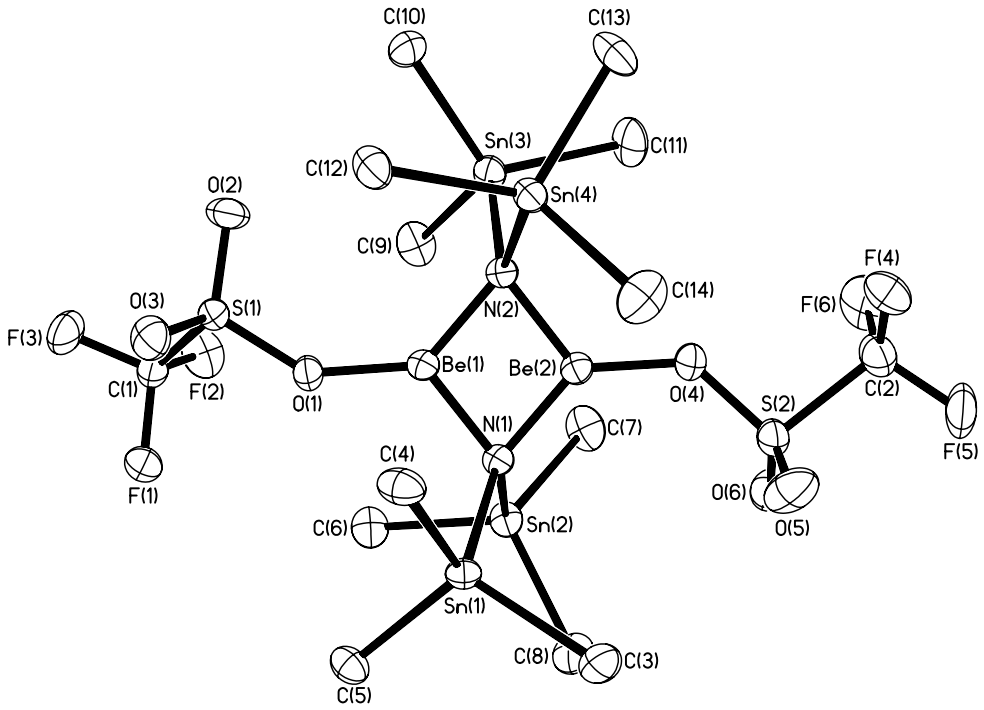



**Figure 2.7**. ORTEP plot representation (30% probability) with numbering scheme for compound **6**. Hydrogen atoms have been omitted for clarity.

All three complexes exist as beryllium dimers in the solid state, with the stannyl or silyl amide acting as a bridging ligand. Chloride ligands and THF molecules attached to the lithium metal centers complete the coordination sphere for **4** and **5**, whereas a triflate ligand completes the coordination sphere for **6**. A summary of the principal interatomic distances and angles for compounds **4-6** is provided in Table 2.2, and a complete list of all distances and angles can be found in Tables A.14, A.18, and A.22 respectively.

**Table 2.2**. Selected average interatomic distances (Å) and angles (degrees) for compounds **4-6.**

| (**4**) | distance/angle | (**5**) | distance/angle | (**6**) | distance/angle |
|---|---|---|---|---|---|
| Sn-N | 2.093(6) | Si-N | 1.756(3) | Sn-N | 2.116(4) |
| Be-N | 1.722(10) | Be-N | 1.707(6) | Be-N | 1.646(7) |
| Be-O | 1.718(10) | Be-O | 1.703(5) | Be-O | 1.550(7) |
| Be-Cl | 2.072(9) | Be-Cl | 2.026(5) | - | - |
| - | - | N-H | 0.920 | - | - |
| Be-N-Be | 79.3(5) | Be-N-Be | 80.9(3) | Be-N-Be | 102.2(4) |
| N-Be-N | 100.7(5) | N-Be-N | 98.7(3) | N-Be-N | 77.8(3) |

Compounds **4-6** are structurally analogous, with all complexes possessing a central $Be_2N_2$ rhombus. Compound **6** is comprised of a more distorted rhombus, as shown by the Be-N-Be and N-Be-N angles listed in Table 2.2. This is likely due to the decreased steric hindrance observed in the three-coordinate beryllium centers of **6**. The beryllium-nitrogen interatomic distances in **4** and **5** are in agreement with the previously reported

beryllium dimer possessing four-coordinate beryllium centers {[$^{i}$Pr$_2$NBe(BH$_4$)]$_2$, Be-N = 1.695 Å and }.[14] The Be-N interatomic distance in **6** is significantly shorter than found for **4** and **5**, due to the decreased coordination on the beryllium(II) metal centers. The Group 14 element-nitrogen interatomic distances were also in the expected range as determined in previous structures containing these bridging amide ligands {[(Me$_3$Sn)$_2$NLi·($^{t}$BuMeO)]$_2$, Sn-N$_{avg}$ = 2.093 Å and [(Me$_3$Si)$_2$NLi·Et$_2$O]$_2$, Si-N$_{avg}$ = 1.705 Å}.[3,11] For compound **5**, the amino hydrogen was assigned from the electron density map, and its presence was verified by the 3300 cm$^{-1}$ stretching frequency in the FT-IR spectrum.

Compound **4** was also structurally characterized by multinuclear NMR techniques. The solution state $^{119}$Sn NMR spectrum contains a single resonance at 75.1 ppm, which is positioned slightly downfield compared to the single resonance at 63.3 ppm for compound **1**. This can be attributed to the fact that the dicationic beryllium metal centers attract more electron density from the nitrogen atoms, thus deshielding the tin atoms. There are also two additional weak resonances found between 50 and 60 ppm, indicating a dynamic behavior in solution. This is also observed in the $^{9}$Be solution state NMR, where a strong single resonance occurs at 13.71 ppm, in agreement with previous studies involving four-coordinate beryllium centers, as well as two additional weak resonances observed upfield from this signal. The occurrence of these additional signals upfield suggests a dynamic equilibrium between solvated and non-solvated solution species, or between monomeric and dimeric structures. In the solid-state $^{9}$Be NMR spectrum a single resonance was observed at approximately 0.3 ppm (Figure 2.8). This

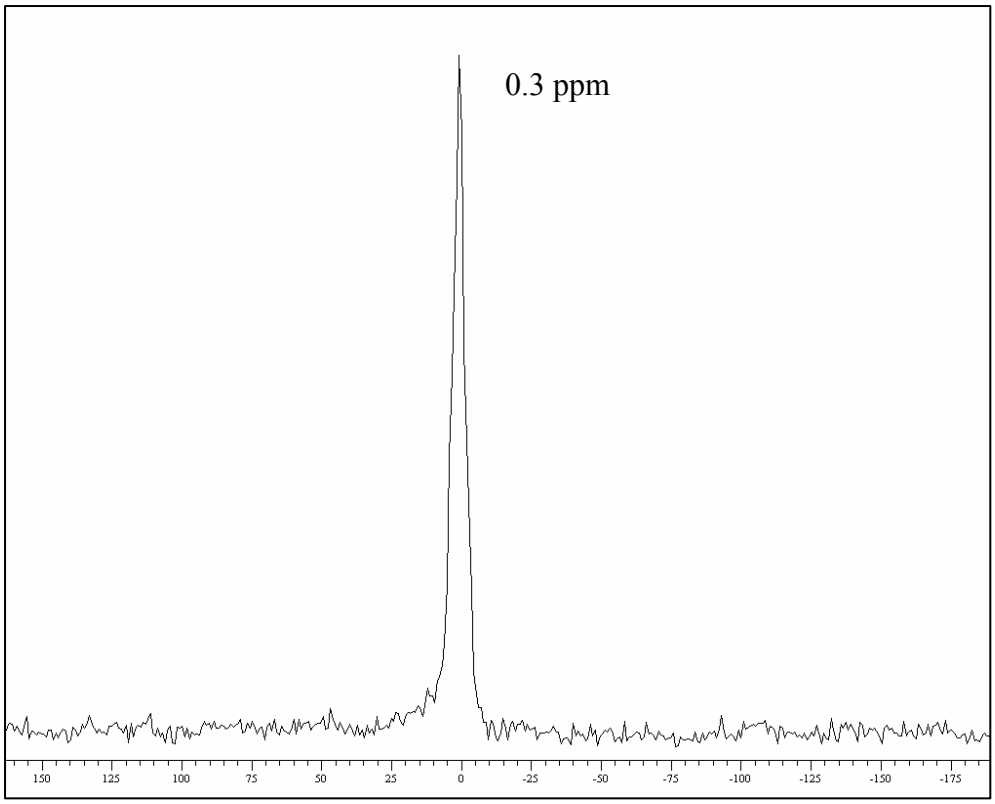



**Figure 2.8**. Solid state $^{9}$Be NMR spectrum of compound **4** (chemical shift scale in ppm).

result substantiates the possibility of dynamic behavior in solution. Due to the limited yield of compounds **5** and **6**, further characterization via multinuclear NMR techniques was limited. However, the dimeric structure of **6** was confirmed by EI-MS techniques. The solid-state structure obtained for **4** via X-ray diffraction techniques was confirmed by the presence of a ($M\text{-}15^{+}$) molecular ion in the EI mass spectrum and by satisfactory elemental analyses.

## Conclusion

In summary, the reaction of compounds **1** and **2** with $BeCl_2$ led to the synthesis and characterization of a new class of beryllium amides. Specifically, compound **4** represents the first structurally characterized example of a beryllium amide possessing stannyl substituents. Additionally, compound **4** was used as a synthon in the preparation of the triflate-coordinated beryllium dimer, **6**. This species opens up further potential exploration of this class of compounds via subsequent ligand exchange reactions.

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# CHAPTER 3

# SYNTHESIS AND CHARACTERIZATION OF LUMINESCENT TETRAMERIC SILVER(I) AMIDES POSSESSING GROUP 14 SUBSTITUENTS: $[(Me_3Si)_2NAg]_4$ and $[(Me_3Sn)(Me_3E)NAg]_4$ (E = Si, Ge, Sn)

## Introduction

Silver(I) coordination compounds have garnered the attention of numerous researchers due to their potential use in sensor technology, application in drug treatment regiments, and their rich photophysical properties.[1] In addition, the nature of argentophilic, $d^{10}$-$d^{10}$ interactions observed in polynuclear silver(I) complexes are of interest from a fundamental standpoint.[2]

Approximately eight years ago, Lappert and coworkers reported a planar, tetranuclear silver(I) amide possessing trimethylsilyl moieties.[3] This compound was accessed through the use of the N-lithio bis(trimethylsilyl)amine precusor and was thought to have opened up an avenue leading to a new class of polynuclear silver complexes. However, until recent work by Rees and Bunge, no analogous silver(I) compounds have been reported.[4] In addition, given the ability of $[(Me_3Sn)_2NLi\bullet THF]_2$ (**1**) to undergo metathesis reactions with $BeCl_2$, it is of interest to determine if similar reaction chemistry can take place with transition metals. Thus, the synthesis and characterization of a series of tetrameric silver(I) amide complexes possessing group 14 substituents, $[(Me_3Si)_2NAg]_4$ (**10**) and $[(Me_3Sn)(Me_3E)NAg]_4$ {E = Si (**8**), Ge (**9**), Sn (**7**)} is described herein.

**Experimental**

All manipulations were carried out in a dry atmosphere glovebox or by standard Schlenk techniques. All solvents were dried over Na metal and were freshly distilled under an inert atmosphere prior to use. AgBr was purchased from Fisher and hexamethyldisilazane was purchased from Aldrich and used without further purification. 10M *n*BuLi was purchased from Aldrich and diluted with hexane. The concentration of the *n*BuLi solution was determined using the procedure reported byGilman.[5] $[(Me_3Sn)_2NLi\bullet(THF)]_2$, $[(Me_3Sn)(Me_3Si)NLi\bullet(Et_2O)]_2$, and $[(Me_3Sn)(Me_3Ge)NLi\bullet(Et_2O)]_2$ were prepared as described in Chapter 2. All NMR experiments were performed on a Bruker 400 MHz Spectrometer at 300K using $C_6D_6$ solvent that was distilled over $CaH_2$ and stored under argon. $^{1}H$, $^{13}C$, and $^{29}Si$ spectra were referenced to TMS. $^{119}Sn$ spectra were externally referenced to $Me_4Sn$. Elemental analyses were performed in triplicate on a Perkin Elmer Series II CHNS/O Analyzer 2400, FT-IR measurements were completed on a Bruker Equinox 55 Spectrometer, mass spectrometry analyses were recorded on a VG Instruments 70SE (Electron Impact ionization; 70eV), and UV/VIS measurements were carried out on a Perkin Elmer UV/VIS/NIR Lambda 19 Spectrometer. All fluorescence measurements were collected on a SPEX Fluorolog Spectrofluorometer equipped with a xenon arc lamp and single grating excitation monochromater. Excited-state lifetimes were measured with a time-correlated single photon counting fluorometer consisting of Photochemical Research Associates flashlamp and optics (PRA Model 510B high-voltage power supply, PRA Model 510B nanosecond lamp, and PRA Model 1200 sample box) and double

monochromators (Istruments SA, Inc., Model H10, on excitation, and Bausch and Lomb, No. 33-86-79, on emission).

*Synthesis of [(Me$_3$Sn)$_2$NAg]$_4$* (**7**): A solution of [(Me$_3$Sn)$_2$NLi•(THF)]$_2$ (0.50 g, 0.59 mmol) in diethyl ether (40 mL) was added dropwise to a diethyl ether slurry of AgBr (0.22 g, 1.19 mmol) at –78°C. The reaction mixture was stirred overnight under an argon atmosphere under light exclusion. The solution was then allowed to attain ambient temperature on its own and it was stirred for an additional 2 hours. The resulting pale yellow solution contained a significant amount of colorless precipitate. The solvent was removed *in vacuo*, the solid residue extracted with 20 mL of hexane, and the resulting slurry filtered to give a clear, golden solution. Colorless crystals were grown from this solution overnight at –40°C. Yield: 0.44 g (83%); $^1$H NMR (400 MHz, C$_6$D$_6$, 25ºC, TMS): $\delta$ 0.45 (s, SnMe$_3$); $^{13}$C NMR (100.6 MHz, C$_6$D$_6$, 25ºC, TMS): $\delta$ 1.03 (s, SnMe$_3$); $^{119}$Sn NMR (149.3 MHz, C$_6$D$_6$, 25ºC, Me$_4$Sn): $\delta$ 100 (s, SnMe$_3$); MS (EI, 451°C): *m/z* 1796 [M$^+$]; elemental analysis calculated (%) for C$_{24}$H$_{72}$N$_4$Sn$_8$Ag$_4$: C 16.03, H 4.04; found: C 16.39, H 4.18.

Crystal data for **7**. C$_{24}$H$_{72}$N$_4$Sn$_8$Ag$_4$: $M_r$ = 1797.86 g cm$^{-3}$, crystal dimensions 0.476 x 0.272 x 0.136 mm, monoclinic, space group *P*2(1)/c, $a$ = 18.355(3), $b$ = 13.010(2) $c$ = 23.107(4) Å, α = 90, $\beta$ = 110.936º; $V$ = 5153.7(15) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 2.317 g cm$^{-3}$, Siemens SMART CCD diffractometer, $1.19 \leq \theta \leq 28.75^{\circ}$, $Mo_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å), $\omega$ scans, $T$ = 193(2) K; of 27,333 measured reflections, 11,907 were independent and 10,280 observed with $I > 2\sigma(I)$, $-24 \leq h \leq 16$, $-17 \leq k \leq 12$, $-30 \leq l \leq 30$; $R_1$ = 0.0617, $wR_2$ = 0.1601, GOF = 1.056 for 409 parameters, $\Delta\rho_{max}$ = 2.052 eÅ$^{-3}$. The structure was solved

by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-97), Lorentz polarization corrections and absorption correction (SADABS) were applied, $\mu$ = 5.303 mm$^{-1}$, min./max. transmission 0.5325/0.1869.

*Synthesis of [(Me$_3$Sn)(Me$_3$Si)NAg]$_4$* (**8**): Compound **8** was prepared in an analogous fashion to compound **7** using [(Me$_3$Sn)(Me$_3$Si)NLi•(Et$_2$O)]$_2$ (0.50 g, 0.75 mmol) and AgBr (0.28 g, 1.50 mmol). Colorless crystals were grown from hexane overnight. Yield: 0.41 g (77%); $^1$H NMR (400 MHz, C$_6$D$_6$, 25ºC, TMS): $\delta$ 0.47 (t, 36H, SiMe$_3$), 0.43 (t, 36H, SnMe$_3$); $^{13}$C NMR (100.6 MHz, C$_6$D$_6$, 25ºC, TMS): $\delta$ 8.53 (s, SiMe$_3$), 0.34 (s, SnMe$_3$); $^{29}$Si NMR (79 MHz, C$_6$D$_6$, 25ºC, Me$_4$Si): $\delta$ 8.21 (s, SiMe$_3$); $^{119}$Sn NMR (149.3 MHz, C$_6$D$_6$, 25ºC, Me$_4$Sn): $\delta$ 75.0 (s, SnMe$_3$); elemental analysis calculated (%) for C$_{24}$H$_{72}$N$_4$Si$_4$Sn$_4$Ag$_4$: C 20.08, H 5.05, N 3.90; found: C 20.00, H 4.57, N 3.95. Crystal data for **8**. C$_{24}$H$_{72}$N$_4$Si$_4$Sn$_4$Ag$_4$: $M_r$ = 1435.46 g cm$^{-3}$, crystal dimensions 0.15 x 0.13 x 0.11 mm, monoclinic, space group *C*2/m, $a$ = 20.708(5), $b$ = 14.095(3) $c$ = 9.550(2) Å, α = 90, $\beta$ = 115.966º; $V$ = 2506.0(10) Å$^3$, $Z$ = 2, $\rho_{calcd}$ = 1.902 g cm$^{-3}$, Siemens SMART CCD diffractometer, 1.81 ≤ $\theta$ ≤ 28.65˚,Mo$_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å), $\omega$ scans, $T$ = 193(2) K; of 7,823 measured reflections, 3,101 were independent and 2,267 observed with $I > 2\sigma(I)$, -16 ≤ $h$ ≤ 26, -16 ≤ $k$ ≤ 18, -12 ≤ $l$ ≤ 11; $R_1$ = 0.0558, $wR_2$ = 0.1608, GOF = 1.107 for 99 parameters, $\Delta\rho_{max}$ = 2.120 eÅ$^{-3}$. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-97), Lorentz polarization corrections and absorption correction (SADABS) were applied, $\mu$ = 3.601 mm$^{-1}$, min./max. transmission 0.6907/0.6178.

*Synthesis of [(Me$_3$Sn)(Me$_3$Ge)NAg]$_4$* (**9**): Compound **9** was prepared in an analogous fashion to compound **7** using [(Me$_3$Sn)(Me$_3$Ge)NLi•(Et$_2$O)]$_2$ (0.50 g, 0.65 mmol) and AgBr (0.24 g, 1.3 mmol). Colorless crystals were grown from hexane overnight. Yield: 0.38 g (73%); $^1$H NMR (400 MHz, C$_6$D$_6$, 25ºC, TMS): $\delta$ 0.55 (t, 36H, GeMe$_3$), 0.45 (t, 36H, SnMe$_3$); $^{13}$C NMR (100.6 MHz, C$_6$D$_6$, 25ºC, TMS): $\delta$ 8.71 (s, GeMe$_3$), 0.49 (s, SnMe$_3$); $^{119}$Sn NMR (149.3 MHz, C$_6$D$_6$, 25ºC, Me$_4$Sn): $\delta$ 84.9 (s, SnMe$_3$); elemental analysis calculated (%) for C$_{24}$H$_{72}$N$_4$Ge$_4$Sn$_4$Ag$_4$: C 17.87, H 4.50, N 3.47; found: C 17.88, H 4.49, N 4.22.

Crystal data for **9**. C$_{24}$H$_{72}$N$_4$Ge$_4$Sn$_4$Ag$_4$: $M_r$ = 1613.46 g cm$^{-3}$, crystal dimensions 0.31 x 0.10 x 0.10 mm, monoclinic, space group *C*2/c, $a$ = 33.982(8), $b$ = 14.182(3) $c$ = 21.170(5) Å, α = 90, $\beta$ = 94.761º; $V$ = 10,167(4) Å$^3$, $Z$ = 8, $\rho_{calcd}$ = 2.108 g cm$^{-3}$, Siemens SMART CCD diffractometer, 1.20 ≤ $\theta$ ≤ 28.65˚,Mo$_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å), $\omega$ scans, $T$ = 193(2) K; of 31,339 measured reflections, 12,011 were independent and 6,927 observed with $I > 2\sigma(I)$, -31 ≤ $h$ ≤ 45, -17 ≤ $k$ ≤ 18, -28 ≤ $l$ ≤ 27; $R_1$ = 0.0806, $wR_2$ = 0.2364, GOF = 1.075 for 409 parameters, $\Delta\rho_{max}$ = 4.900 eÅ$^{-3}$. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-97), Lorentz polarization corrections and absorption correction (SADABS) were applied, $\mu$ = 5.775 mm$^{-1}$, min./max. transmission 0.5904/0.2710.

*Synthesis of [(Me$_3$Si)$_2$NAg]$_4$* (**10**): *N*-lithio bis(trimethylsilyl)amine was prepared by adding 3.10 mL of *n*BuLi (1.6 M solution in hexane) to a diethyl ether solution of (Me$_3$Si)$_2$NH (0.80 g, 4.9 mmol) at 0°C. The solution was allowed to attain ambient temperature on its own and it was subsequently stirred for 2 hours under an argon atmosphere. This solution was added dropwise to a diethyl ether slurry of AgBr (0.92 g,

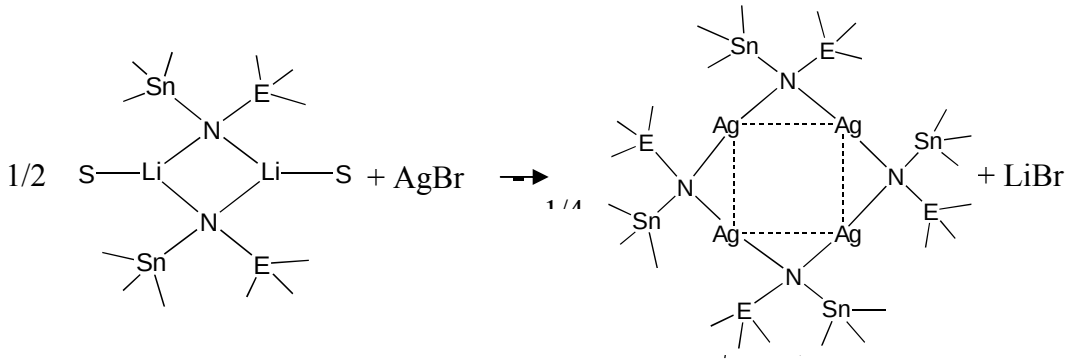
4.9 mmol) at –78°C and it was stirred overnight under an argon atmosphere under light exclusion. The reaction mixture was then allowed to attain ambient temperature and it was stirred for an additional 3 hours. The resulting pale yellow solution contained a significant amount of colorless precipitate. The solvent was removed *in vacuo*, the solid residue extracted with 30 mL of hexane, and the resulting slurry filtered to yield a clear, golden solution. Colorless crystals were grown overnight at –40°C. Yield: 0.33 g (66%); $^{1}$H NMR (400 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ 0.55 (s, $SiMe_3$); $^{13}$C NMR (100.6 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ 8.71 (s, $SiMe_3$); MS (EI, 267°C): *m/z* 1057 [$(M-15)^+$]. Crystal data for **10**. $C_{24}H_{72}N_4Si_8Ag_4$: $M_r$ = 1073.06 g cm$^{-3}$, crystal dimensions 0.25 x 0.14 x 0.10 mm, monoclinic, space group *P*2/*n*, *a* = 9.2069(15), *b* = 13.807(2), *c* = 17.664(2) Å, α = 90, $\beta$ = 91.245º; *V* = 2319.1(7) Å$^3$, *Z* = 2, $\rho_{calcd}$ = 1.537 g cm$^{-3}$, Siemens SMART CCD diffractometer, 1.85 ≤ $\theta$ ≤ 28.74°,$Mo_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å), $\omega$ scans, *T* = 193(2) K; of 14,415 measured reflections, 5,483 were independent and 3,585 observed with $I > 2\sigma(I)$, -10 ≤ *h* ≤ 12, -18 ≤ *k* ≤ 16, -23 ≤ *l* ≤ 24; $R_1$ = 0.0238, $wR_2$ = 0.0574, GOF = 1.076 for 207 parameters, $\Delta\rho_{max}$ = 0.419 eÅ$^{-3}$. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-97), Lorentz polarization corrections and absorption correction (SADABS) were applied, $\mu$ = 1.890 mm$^{-1}$, min./max. transmission 0.8306/0.6443.

**Results and Discussion**

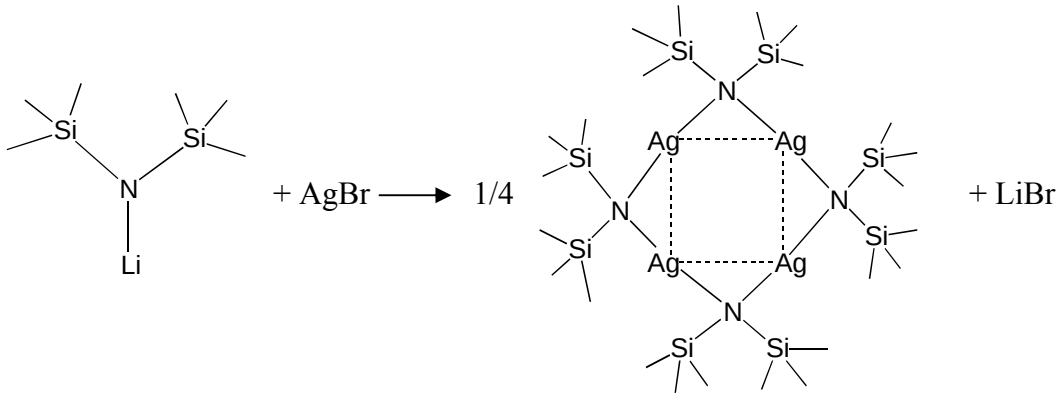
*Synthesis*

The synthesis of compounds **7-9** is depicted in Schemes 3.1. Compounds **7-9** were prepared by adding an ether solution of the appropriate lithiated stannylamine

(compounds **1**-**3**) to an ether slurry of AgBr at –78ºC. The reaction mixture was stirred overnight at this temperature before allowing to attain ambient temperature. The solvent was removed *in vacuo*, the solid residue extracted with hexane, and the LiBr precipitate filtered off. Colorless crystals were grown at –40ºC. Compound **10** was synthesized in a similar fashion; however, the *N*-lithio bis(trimethylsilyl)amine was generated *in situ* before being reacted with AgBr.




E = Sn (**7**), Si (**8**), Ge(**9**)
S = THF, $Et_20$




(**10**)

**Scheme 3.1**. Synthesis of compounds **7-10.**

*Characterization*

Crystals of compounds **7**-**10** were analysed by single crystal X-ray diffraction and the crystal structures of these compounds are depicted in Figures 3.1-3.4.

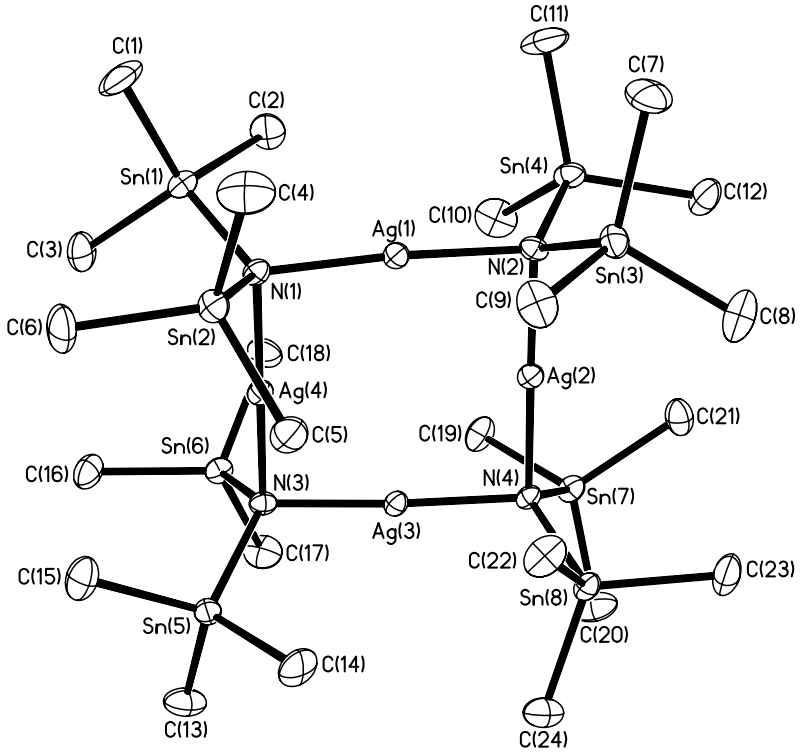



**Figure 3.1**. ORTEP plot representation (30% probability) with numbering scheme for compound **7**. Hydrogen atoms have been omitted for clarity.

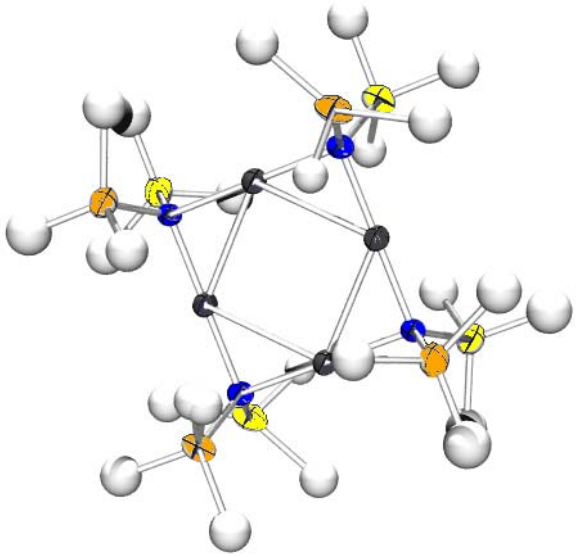


**Figure 3.2**. ORTEP plot representation (30% probability) for compound **8**. Hydrogen atoms have been omitted for clarity.

Sn ○ N ● Ag ● Si ●

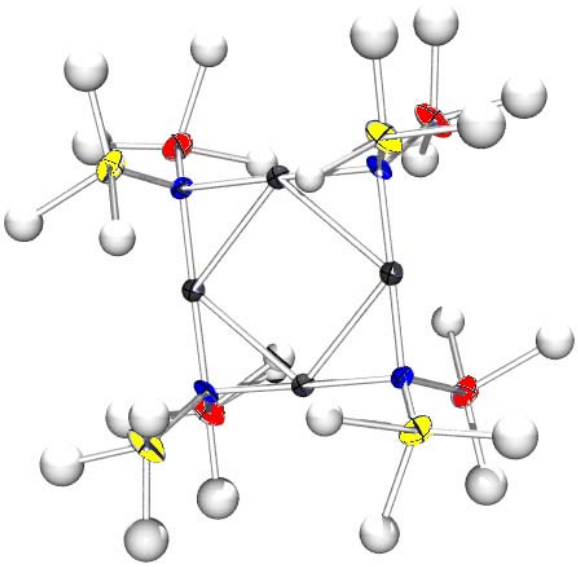


**Figure 3.3**. ORTEP plot representation (30% probability) for compound **9**. Hydrogen atoms have been omitted for clarity.

Sn ● N ● Ag ● Ge ●

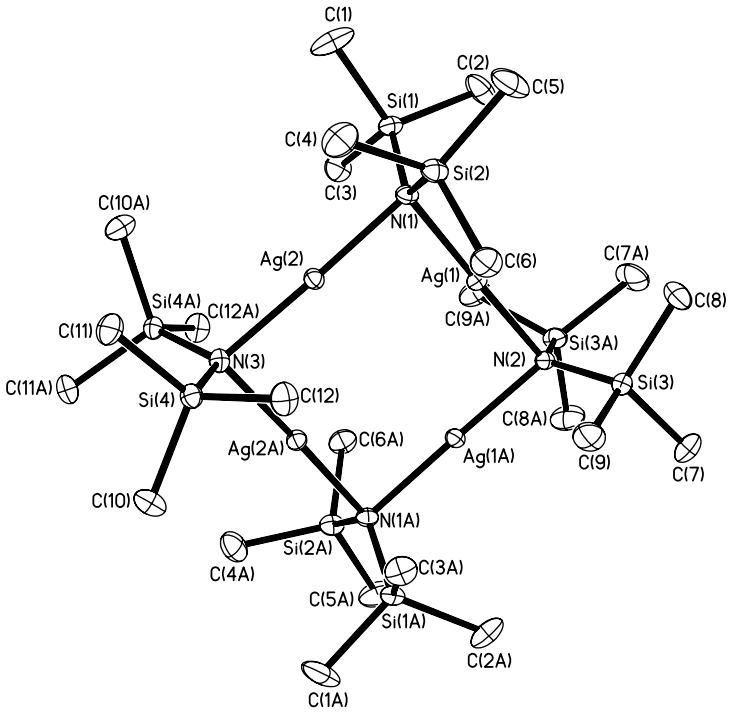



**Figure 3.4**. ORTEP plot representation (30% probability) with numbering scheme for compound **10**. Hydrogen atoms have been omitted for clarity.

All four complexes exist as tetramers in the solid state, comprised of a nearly planar $Ag_4N_4$ core, with each amido ligand bridging two silver metal centers. The predominant feature of these complexes are close interactions observed between silver(I) cations, found to be less than the sum of the van der Waals radii for $Ag^+$ ions (< 3.4 Å). A summary of the principal interatomic distances and angles for compounds **7-10** is provided in Table 3.1 and a complete list of all distances and angles can be found in Tables A.26, A.30, A.33, and A.36, respectively.

**Table 3.1**. Selected average interatomic distances (Å) and angles (degrees) for compounds **7-10.**

| (**7**) | Distance/ angle | (**8**) | Distance/ angle | (**9**) | Distance/ angle | (**10**) | Distance/ angle |
|---|---|---|---|---|---|---|---|
| Sn-N | 2.053(6) | Sn/Si-N | 1.959(6) | Sn/Ge-N | 1.9562(6) | Si-N | 1.747(15) |
| Ag-N | 2.0994(6) | Ag-N | 2.125(5) | Ag-N | 2.1125(5) | Ag-N | 2.145(2) |
| Ag-Ag | 3.0024(8) | Ag-Ag | 3.0026(14) | Ag-Ag | 3.0112(10) | Ag-Ag | 3.0087(6) |
| N-Ag-N | 177.6(2) | N-Ag-N | 179.7(2) | N-Ag-N | 178.9(2) | N-Ag-N | 178.76(7) |
| Ag-N-Ag-N | 177.34 | Ag-N-Ag-N | 179.71 | Ag-N-Ag-N | 178.89 | Ag-N-Ag-N | 178.76 |

The $Ag_4N_4$ core is structurally analogous to the bis(trimethylsilyl)amido complex reported by Lappert *et al*.[3] and to the more recent tetramethyl guanidine complexes reported in our laboratory.[4] Compounds **7-10**, in a similar fashion to these previously reported structures, possess nearly planar metal-nitrogen cores (the Ag-N-Ag-N dihedral angles are summarized in Table 3.1) and nearly linear N-Ag-N angles.

Similar to the trend observed for the Li-N interatomic distance in compounds **1-3**, the Ag-N distance decreases with increasing molecular weight of the second amide

substituent (heavier Group 14 element). The Sn-N distances in compound **7** are observed to be in the expected range found for other trimethylstannyl amides.[6,7] However, in compounds **8** and **9**, the tin atom was crystallographically indistinguishable from silicon and germanium atoms, respectively. In a similar fashion to compounds **2** and **3**, the observed Sn/Si- and Sn/Ge-N interatomic distances fall between the distances typically observed for Sn-N and Si-N or Ge-N. The presence of silicon and germanium in compounds **8** and **9** was verified by the $^{119}$Sn NMR chemical shifts for the two compounds (Figure 3.5) and the elemental analyses.

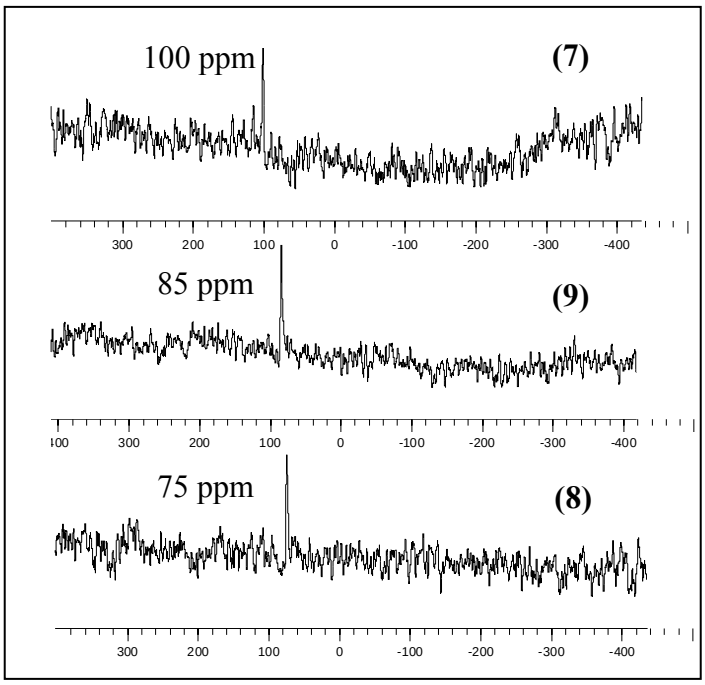



**Figure 3.5**. $^{119}$Sn spectra for compounds **7-9** (chemical shift scale in ppm).

Perhaps the most notable feature of compounds **7-10** is the close contact observed for the silver(I) ions. As previously mentioned, the Ag-Ag distances are shorter than the

sum of the van der Waals radii, indicating the presence of a $d^{10}$-$d^{10}$ closed shell interaction. This argentophilic interaction is believed to have a similar origin to commonly observed aurophilicity found in polynuclear gold(I) complexes. However, since the strength of the $Ag^{+}$-$Ag^{+}$ closed shell interaction has been determined to be of a lesser magnitude than that for $Au^{+}$-$Au^{+}$ (aurophilic interactions have been found to be of a similar energy as hydrogen bonds, whereas argentophilic contacts are about the same energy as standard van der Waals interactions), the occurrence of argentophilicity in silver complexes is less favored, and hence, less commonly observed.[8]

Theoretically, in the absence of (*n*+1)s and (*n*+1)p orbitals, the interaction between closed-shell $d^{10}$ centers is repulsive in nature. However, mixing of the filled *n*d-orbitals with these empty orbitals derived from higher energy [(*n*+1)s and (*n*+1)p] results in metal-metal interactions. It is noted though, that the observation of short metal-metal contacts in such systems does not necessarily mean that a metal-metal bond exists, so the nature of the bridging ligands and their effect on the oligomerization of the metal centers needs to be taken into account. If indeed a metal-metal bond is formed, unique photophysical properties are often observed. In polynuclear silver(I) complexes, the origin of the emission has been assigned to dσ*-pσ, dσ*-s, and mixed-metal-centered, metal-to-ligand charge transfer (MLCT) transitions.[2] The absorption and emission spectra were obtained for compounds **7** and **8**, as well as the previously reported compound **10** with the aim of determining whether these compounds might provide an entry point for future studies on the nature of argentophilic, $d^{10}$-$d^{10}$ interactions. The absorption, emission, and excitation spectra, along with the emission decay for compound **7** are shown in Figure 3.6. In addition, theoretical calculations were performed on a high

symmetry model of compound **7**, and graphical representations of the frontier orbitals for this model complex are illustrated in Figure 3.7 [The geometry of **7** was optimised using Density Functional Theory (DFT). The B3LYP method was employed with the LACVP* basis set. The model compound was found to have $C_{2h}$ symmetry. The single point energy calculation used to generate the HOMO and LUMO surfaces was performed using the same method and basis set.]

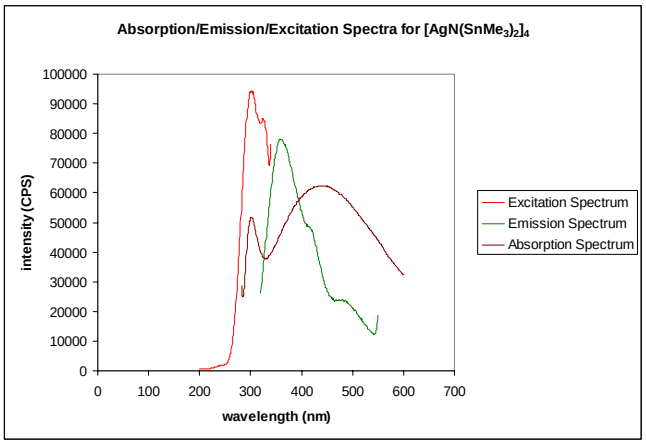



**Figure 3.6.A**. The UV/VIS aborption, emisson (@ 300 nm), and excitation (@ 350 nm) spectra for compound **7** in hexane.

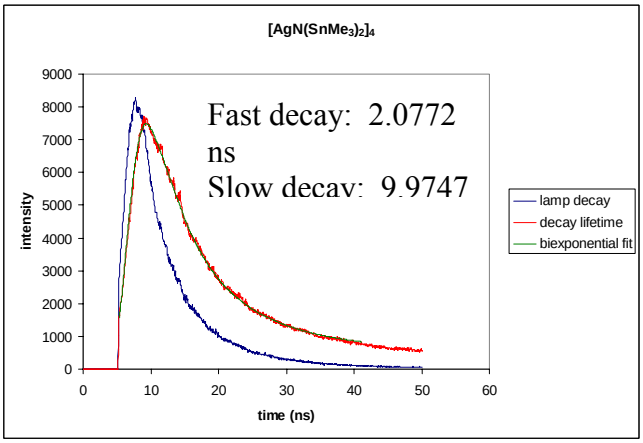



**Figure 3.6.B**. Emission decay for compound **7** in hexane (excitation @ 216 nm and emission @ 365).

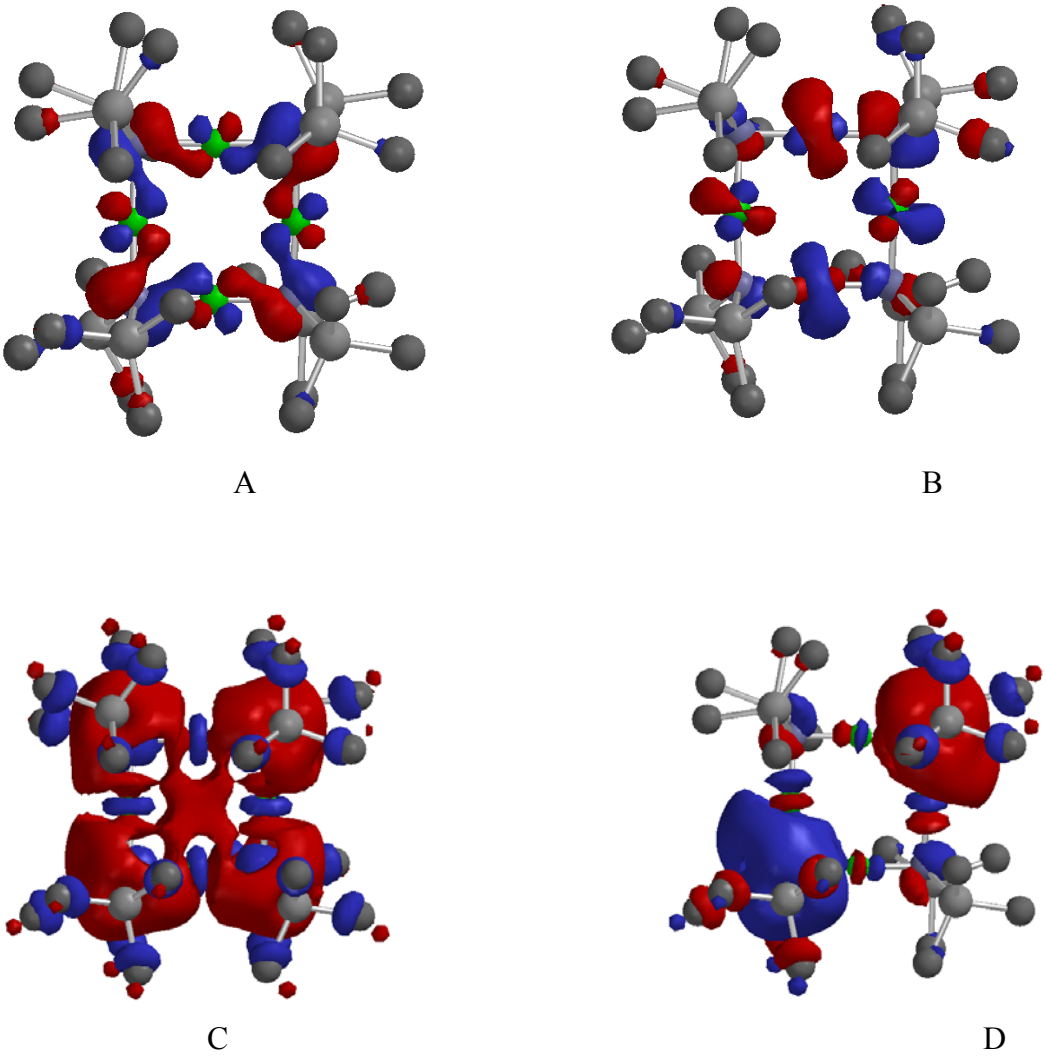



**Figure 3.7**. A: HOMO; B: HOMO(-1); C: LUMO; D: LUMO(-1) for compound **7** from DFT theoretical calculations.

As seen in Figure 3.6, compound **7** exhibits a sharp absorption at 298 nm, along with an additional broad absorption at 432 nm. Upon excitation at 300 nm, the complex intensely emitted at 365 nm and displayed vibronically structured bands located at 421 and 489 nm. The excitation spectrum was obtained by irradiating the complex at 365 nm and the maximum excitation peak was found at 305 nm. The emission decay was also collected and found to undergo biexponential decay, with the fast decay occurring in 2.0 ns and the slow decay in 9.9 ns. Photophysical studies were also performed for compounds **8** and **10**. Table 3.2 summarizes the results for compounds **7**, **8**, and **10**.

**Table 3.2**. UV/VIS absorption, emission, excitation, and decay lifetime for compounds **7**,**8**, and **10**.

| | **7** | **8** | **10** |
|---|---|---|---|
| **$\lambda_{max}$ (nm)** | 298, 432 | 256, 438 | 265, 420 |
| emission (nm) | (@ 300 nm)<br>365, 421, 489 | (@ 266 nm)<br>378, 420, | (@ 297 nm)<br>365, 424, 491 |
| excitation (nm) | (@ 365 nm)<br>305 | (@ 365 nm)<br>306 | (@ 360 nm)<br>308 |
| lifetime (ns)<br>excitation @ 315 nm<br>emission @ 365 nm | $\tau_1$ = 2.0 (fast)<br>$\tau_2$ = 9.9 (slow) | $\tau_1$ = 2.1 (fast)<br>$\tau_2$ = 10.4 (slow) | $\tau_1$ = 2.0 (fast)<br>$\tau_2$ = 9.7(slow) |

Though the spectroscopic results reported here do not conclusively indicate emission from a metal centered excited state, it is possible such a phenomenon is occurring in compounds **7**, **8**, and **10**. For compound **7**, the lower energy absorption band at 432 nm is likely due to a ligand-to-metal charge transfer (LMCT) and the higher energy band at 298

nm possibly arises from the population of a metal-centered excited state, expected to occur at higher energy than a LMCT transition. The potential for emission from metal-centered excited states is corroborated by the results of the theoretical calculations shown in Figure 3.7. The nature of the frontier orbitals indicates that there is indeed some electronic communication between the $Ag^+$ metal centers. This suggests that the emission may originate from excited states that are at least partially centered on the metal cations. However, more detailed photophysical studies, such as low temperature emission studies and the determination of the quantum yield, as well as excited state theoretical calculations would lend more insight into the nature of the emission processes observed in these tetranuclear complexes.

**Conclusion**

The planar, tetrameric silver-nitrogen core found in the silver(I) bis(trimethylsilyl)amide complex previously reported was believed to be a forerunner to a new class of silver amides.[3] However, until recent work in our laboratory, no further progress in this area had been accomplished.[4] This report extends the family of tetrameric amidosilver complexes via the use of homoleptic and heteroleptic lithiated stannyl amines. Compounds **7-9** were synthesized and fully characterized by single crystal X-ray diffraction experiments, as well as multinuclear NMR techniques. In addition, compounds **7**, **8**, and the previously reported compound **10** were analyzed by spectroscopic methods in an attempt to probe the nature of their photophysical properties. It was concluded that the close Ag-Ag interactions observed in these compounds result in emission that potentially originates from metal-centered excited states. More detailed

photophysical studies and excited state calculations, which would provide additional insight into the nature of the emission phenomena are warranted.

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# CHAPTER 4

# SYNTHESIS AND STRUCTURAL DETERMINATION OF DIMERIC ZINC(II) AND ZIRCONIUM(IV) AMIDES: $[Zn\{N(SnMe_3)_2\}(Cl)_2 \bullet Li(Et_2O)_2]_2$ AND $[(C_5H_5)_2ZrNSnMe_3]_2$

## Introduction

Zinc and zirconium amides have previously been synthesized and employed as precursors in the MOCVD of zinc nitride[1] and atomic layer deposition (ALD) of zirconium oxide[2], respectively. In the scope of this work, the synthesis and structural characterization of zinc(II) and zirconium(IV) amides is desired in order to further explore the use of the lithiated bis(trimethylstannyl)amine as a synthon to new transition metal complexes. In addition, it is of interest to synthesize heterometallic zirconium-tin complexes that may be used as "same-source" precursors for ZTT via MOCVD.

The reaction of zinc and zirconium halides with *N*-lithio bis(trimethylstannyl)amine (**1**) was examined. The isolated metal amide dimers, $[Zn\{N(SnMe_3)_2\}(Cl)_2 \bullet Li(Et_2O)_2]_2$ (**11**) and $[(C_5H_5)_2ZrNSnMe_3]_2$ (**12**) represent the first structurally characterized zinc amido and zirconium imido compounds possessing the trimethylstannyl moiety.

## Experimental

All manipulations were carried out in a dry atmosphere glovebox or by standard Schlenk techniques. All solvents were dried over Na° metal and were freshly distilled under an inert atmosphere prior to use. $ZnCl_2$ and $(C_5H_5)_2ZrCl_2$ reagents were purchased from

Alfa Aesar and used without further purification. $[(Me_3Sn)_2NLi\bullet(THF)]_2$ was prepared as described in Chapter 2.

*Synthesis of [Zn{N(SnMe$_3$)$_2$}(Cl)$_2$•Li(Et$_2$O)$_2$]$_2$* (**11**): A solution of $[(Me_3Sn)_2NLi\bullet(THF)]_2$ (1.00 g, 1.19 mmol) in diethyl ether (40 mL) was added to a diethyl ether slurry of $ZnCl_2$ (0.19 g, 2.38 mmol) in a dropwise fashion at 0°C. The reaction mixture was allowed to attain ambient temperature on its own whereby a colorless precipitate formed within 10 minutes. After stirring overnight under an argon atmosphere the reaction mixture was filtered and its volume subsequently reduced, *in vacuo*, to about 30 mL. Colorless crystals were grown at –40°C over a two-day period.

Crystal data for **11**. $C_{28}H_{76}N_2O_4Cl_4Sn_4Zn_2$: $M_r$ = 1266.09 g cm$^{-3}$, crystal dimensions 0.15 x 0.14 x 0.14 mm, triclinic, space group *P*-1, $a$ = 11.990(3), $b$ = 12.044(3), $c$ = 20.926(4) Å, α = 83.604(4), $\beta$ = 76.341(4), γ = 61.753(4)º; $V$ = 2586.8(9) Å$^3$, $Z$ = 2, $\rho_{calcd}$ = 1.625 g cm$^{-3}$, Siemens SMART CCD diffractometer, $1.00 \leq \theta \leq 25.05^{\circ}$. $Mo_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å), $\omega$ scans, $T$ = 193(2) K; of 13,749 measured reflections, 9,092 were independent and 5,631 observed with $I > 2\sigma(I)$, $-14 \leq h \leq 10$, $-14 \leq k \leq 14$, $-24 \leq l \leq 22$; $R_1$ = 0.0701, $wR_2$ = 0.1596, GOF = 1.029for 438 parameters, $\Delta\rho_{max}$ = 1.420 eÅ$^{-3}$. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-97), Lorentz polarization corrections and absorption correction (SADABS) were applied, $\mu$ = 3.047 mm$^{-1}$, min./max. transmission 0.6820/0.6528.

*Synthesis of [$(C_5H_5)_2ZrNSnMe_3]_2$* (**12**): A solution of $[(Me_3Sn)_2NLi\bullet(THF)]_2$ (1.00 g, 1.19 mmol) in diethyl ether (40 mL) was added to a diethyl ether slurry of $(C_5H_5)_2ZrCl_2$ (0.19 g, 2.38 mmol) in a dropwise fashion at 0°C. The reaction mixture was allowed to attain ambient temperature on its own whereby a colorless precipitate formed within 10 minutes. After stirring overnight under an argon atmosphere the reaction mixture was filtered and its volume reduced, *in vacuo*, to about 30 mL. Yellow crystals were grown at –80°C over a two-day period.

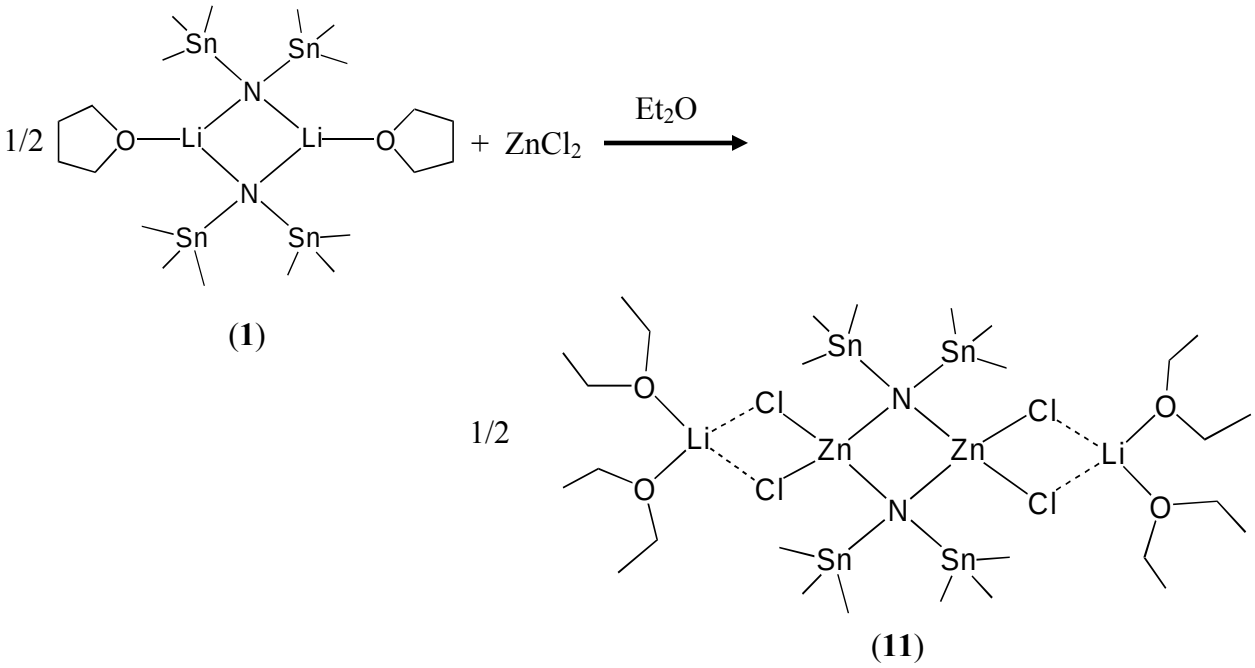
Crystal data for **12**. $C_{26}H_{38}N_2Sn_2Zr_2$: $M_r$ = 798.40 g cm$^{-3}$, crystal dimensions 0.34 x 0.20 x 0.07 mm, monoclinic, space group *P*2(1)/n, $a$ = 8.2519(5), $b$ = 16.2209(11), $c$ = 10.3432(7) Å, α = 90, $\beta$ = 98.5650(10)º; $V$ = 1369.03(16) Å$^3$, $Z$ = 2, $\rho_{calcd}$ = 1.937 g cm$^{-3}$, Siemens SMART CCD diffractometer, $2.35 \leq \theta \leq 28.80^{\circ}$. $Mo_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å), $\omega$ scans, $T$ = 193(2) K; of 8,762 measured reflections, 3265 were independent and 2,137 observed with $I > 2\sigma(I)$, $-11 \leq h \leq 9$, $-20 \leq k \leq 19$, $-12 \leq l \leq 13$; $R_1$ = 0.0406, $wR_2$ = 0.0935, GOF = 0.964 for 161 parameters, $\Delta\rho_{max}$ = 0.969 eÅ$^{-3}$. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-97), Lorentz polarization corrections and absorption correction (SADABS) were applied, $\mu$ = 2.560 mm$^{-1}$, min./max. transmission 0.8452/0.4765.

## Results and Discussion

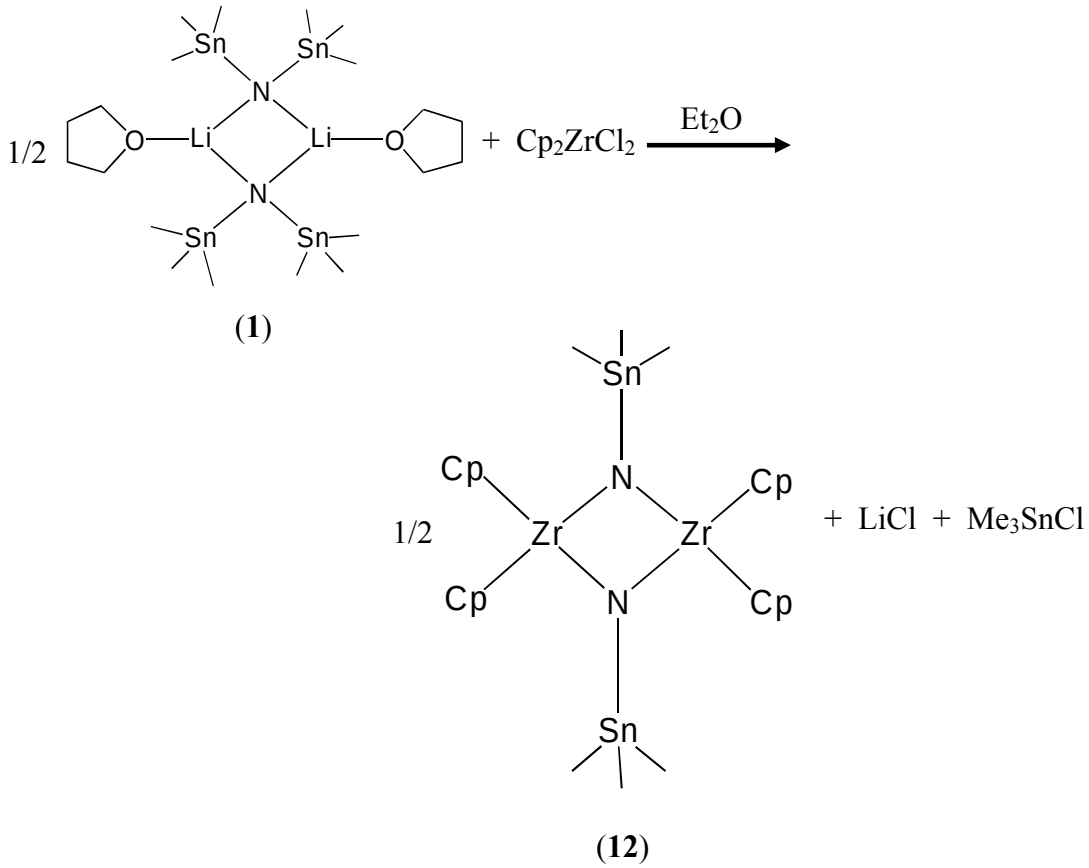
*Synthesis*

The synthesis of compounds **11** and **12** is illustrated in Schemes 4.1 and 4.2, respectively. Both complexes were prepared by reacting the appropriate metal halide starting material with 0.5 equivalents of **1**. The reaction mixtures were stirred overnight and the resulting

solutions were filtered. Crystals of each compound were obtained directly from the mother liquor (compound **11**: colorless crystals at –40ºC; compound **12**: yellow crystals at –80ºC).




**Scheme 4.1**. Synthesis of compound **11.**




**Scheme 4.2**: Synthesis of compound **12.**

A comparison of the reactions in Schemes 4.1 and 4.2 to those discussed in Chapters 2 (**1** + $BeCl_2$) and 3 (**1** + AgBr) indicates that the metal chlorides react with the lithiated bis(trimethylstannyl)amine in a different fashion. In the case of Zn, instead of producing an equivalent of lithium halide and the corresponding oligomeric coordination complex possessing the bridging bis(stannyl)amide moiety, an "ate" complex forms that retains both chloride ligands in the coordination sphere. When the bis(cyclopentyldienyl)zirconium dichloride is utilized, a metal dimer possessing a bridging stannylimide ligand is obtained. In addition, both lithium chloride and

trimethyltin chloride are formed as co-products. A potential explanation for the formation of compound **12** and trimethyltin chloride as a by-product is the increased lability of the Zr-Cl bond in $Cp_2ZrCl_2$ (Zr-Cl interatomic distance = 2.6 Å) in comparison to $BeCl_2$ and $ZnCl_2$ (Be-Cl interatomic distance = 2.2 Å and Zn-Cl interatomic distance = 2.2 Å). A literature search has concluded that no prior metathesis reaction involving the elimination of both LiCl and $Me_3SnCl$ has been observed.

*Characterization*

The molecular structures of compounds **11** and **12,** determined by single crystal X-ray diffraction are depicted in Figures 4.1 and 4.2.

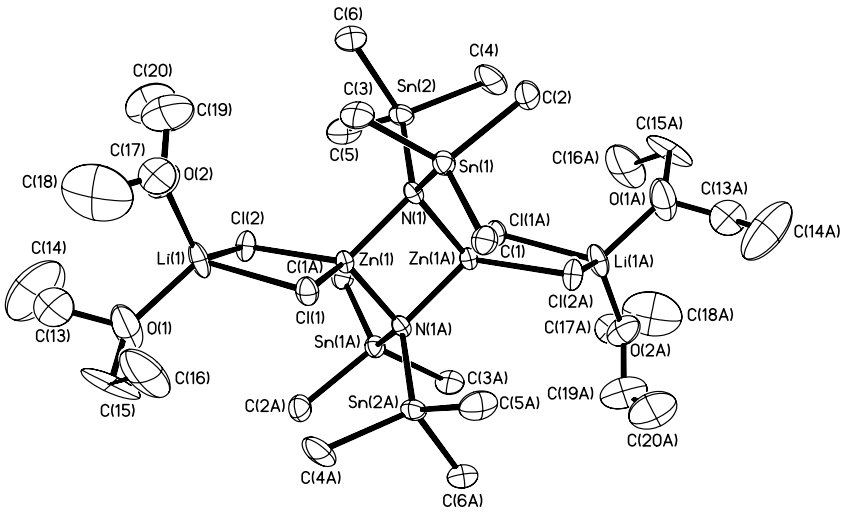



**Figure 4.1**. ORTEP plot representation (30% probability) with numbering scheme for compound **11**. Hydrogen atoms have been omitted for clarity.

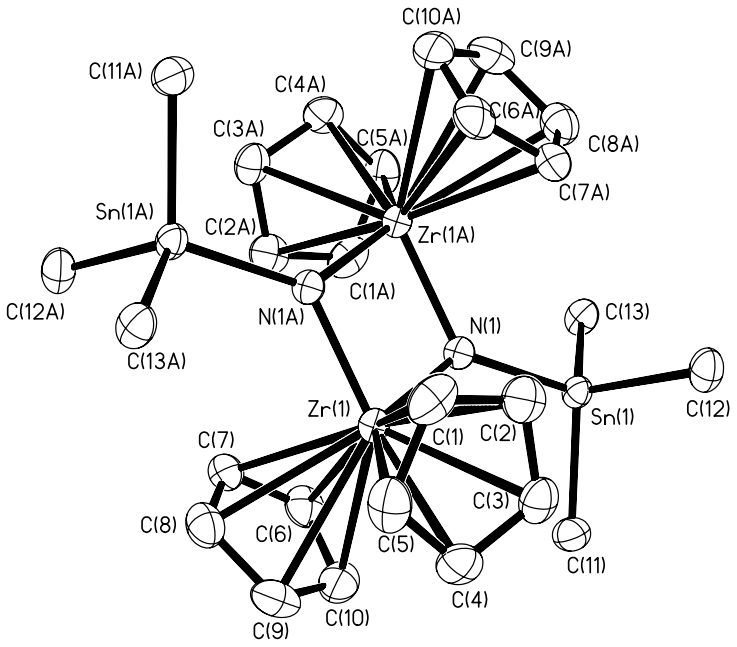



**Figure 4.2**. ORTEP plot representation (30% probability) with numbering scheme for compound **12**. Hydrogen atoms have been omitted for clarity.

Compounds **11** and **12** both exist as dimers in the solid state and are comprised of $M_2N_2$ rhomboid cores. Table 4.1 lists the pertinent interatomic distances and angles for **11** and **12**, and complete lists of all angles and distances for these two structures are located in Tables A.40 and A.44, respectively.

**Table 4.1**. Selected average interatomic distances (Å) and angles (degrees) for compounds **11** and **12**.

| (**11**) | distance/angle | (**12**) | distance/angle |
|---|---|---|---|
| Sn-N | 2.087(8) | Sn-N | 2.047(4) |
| Zn-N | 2.023(8) | Zr-N | 2.059(4) |
| Zn-Cl | 2.315(3) | Zr-C | 2.603(6) |
| N-Zn-N | 96.3(3) | N-Zr-N | 80.95(17) |
| Zn-N-Zn | 83.6(3) | Zr-N-Zr | 99.05(17) |

Compound **11** represents the first structurally characterized zinc amide "ate" complex. It possesses a dimeric $Zn_2N_2$ core, with bridging bis(stannylamide) ligands and terminal chloride ligands. The Sn-N interatomic distance is in the range observed for compounds **1**, **4**, and **6**, and the Zn-N distance is similar to that found previously in other zinc amide dimers $\{[ZnN[Si(CH_3)CH_2CH_2Si(CH_3)_2]]_2$, $Zn\text{-}N_{bridging} = 2.065$ Å$\}$.[3] As is expected in an "ate" complex, the Zn-Cl interatomic distance is longer than the predicted Zn-Cl distance in $ZnCl_2$ (approximately 2.2 Å). Additionally, the acute M-N-M and obtuse N-M-N angles are found in compounds **1**-**5** as well.

The dimeric compound **12** possesses zirconium(IV) metal centers bridged by trimethylstannyl imido units and terminally coordinated by cyclopentadienyl ligands. The Sn-N distance found in **12** is slightly shorter than in compounds **4**, **7**, and **11**, due to the fact that only one trimethylstannyl moiety is bound to the nitrogen. The observed Zr-N distance corresponds well with Zr-N distances found in other zirconium amide dimers {$[Cp_2ZrN(Ph^tBu)]_2$, Zr-N = 2.096 Å}.[4] The obtuse M-N-M and the acute N-M-N angles are in contrast to the observed angles in compounds **1**-**5** and **11**. This likely can be attributed to the decreased steric hindrance around the bridging nitrogen.

## Conclusions

The initial account on the synthesis and structural characterization of zinc and zirconium complexes containing stannylamine or stannylimine ligands is reported. In addition, both compounds exemplify the first zinc amide "ate" and the first metal amide complex synthesized via a metathesis reaction involving the elimination of LiCl and $Me_3SnCl$ (**11** and **12**, respectively). The successful synthesis and characterization of compound **12** emphasizes the significance of **1** as a synthon to heterometallic coordination compounds that can potentially be employed as ZTT precursors in MOCVD processes.

## References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# CHAPTER 5

# DESIGN AND SYNTHESIS OF GROUP 14-NITROGEN HETEROCUBANES

## SECTION A: SYNTHESIS AND CHARACTERIZATION OF A SERIES OF GROUP 14-NITROGEN HETEROCUBANES: $[M(\mu_3\text{-}NSiMe_3)]_4$ (M = Ge, Sn, Pb)

### Introduction

After establishing that the reaction of $[(Me_3Sn)_2NLi\bullet(THF)]_2$ (**1**) with $Cp_2ZrCl_2$ yields both LiCl and $Me_3SnCl$ as by-products (Chapter 4), it was of interest to determine whether dicationic metal species analogously generate LiCl and $Me_3SnCl$ upon reaction with $[(Me_3Sn)(Me_3E)NLi\bullet THF]_2$ {E = Si(**2**), Ge(**3**), Sn(**1**)}, and if so, what type of oligomeric metal complex might be formed.

Since tin amides may be useful precursors in the MOCVD of ZTT,[1] initial experiments investigated the reaction of $SnCl_2$ with compound **2**. The results indicate that LiCl and $Me_3SnCl$ do indeed form as by-products in the reaction, while a tetrameric tin-nitrogen heterocubane possessing exo-cube silicon moieties is generated as the primary product (see Scheme 5.1). Since the cubane structural motif has previously been used by Barron, *et al*., in the molecular design of gallium sulfide precursors[2] for utilization in MOCVD processes, the utility of these tin-nitrogen cubanes in the MOCVD of ZTT needs to be explored. The implemented molecular design strategy sought to exhibit control over the identity of the divalent metal cation located in the cube, as well as the tetravalent atom bound to nitrogen in the exo-cube position. The exploration of this design concept will be summarized in this chapter, and specifically, this sub-chapter

explores the modification of the endo-cube metal, resulting in the synthesis and characterization of the three compounds, $[M(\mu_3\text{-}NSiMe_3)]_4$ [M = Sn (**13**), Ge (**14**), Pb (**15**)]

**Experimental**

All manipulations were carried out in a dry atmosphere glovebox or by standard Schlenk techniques. All solvents were dried over Na° metal or $P_2O_5$ ($CH_2Cl_2$) and were freshly distilled under an inert atmosphere prior to use. $SnCl_2$ and $PbCl_2$ reagents were purchased from Alfa Aesar and used without further purification. $[(Me_3Sn)(Me_3Si)NLi\bullet(Et_2O)]_2$ was prepared as described in Chapter 2 and $GeCl_2\cdot(dioxane)$[3] was prepared according to literature procedures. All NMR experiments were performed on a Bruker 400 MHz Spectrometer at 300K using $C_6D_6$ solvent that was distilled over $CaH_2$ and stored under argon. $^1H$ and $^{13}C$ spectra were referenced to TMS. $^{119}Sn$ spectra were externally referenced to $Me_4Sn$. Elemental analyses were performed in triplicate on a Perkin Elmer Series II CHNS/O Analyzer 2400, FT-IR measurements were performed on a Bruker Equinox 55 Spectrometer, mass spectrometry analyses were done on a VG Instruments 70SE (Electron Impact; 70eV), and UV/VIS measurements were performed on a Perkin Elmer UV/VIS/NIR Lambda 19 Spectrometer. All TGA experiments were performed on a Perkin Elmer 7/DX thermal analyser interfaced to a Perkin Elmer Thermal Analysis Controller (TAC). The instrument is housed in a dry atmosphere glovebox. Argon was used as the purge gas and all %weight vs. temperature profiles were done at a 10°C/min. temperature ramp under ambient pressure.

*Synthesis of [Sn($\mu_3$-NSiMe$_3$)]$_4$* (**13**): A sample of [(Me$_3$Sn)(Me$_3$Si)NLi•(Et$_2$O)]$_2$ (0.75 g, 1.13 mmol) was dissolved in diethyl ether (40 mL) and the solution was added to a diethyl ether slurry of $SnCl_2$ (0.42 g, 2.26 mmol) in a dropwise fashion at 0°C. The reaction mixture was allowed to attain ambient temperature on its own and a colorless precipitate formed within 10 minutes. The solution was stirred overnight under an argon atmosphere and the reaction mixture was subsequently filtered through a Schlenk frit. The solvent was removed *in vacuo* and the orange solid residue was extracted with 15 mL of $CH_2Cl_2$. Orange crystals were grown from this solution at –80°C over a two-day period. Yield: 0.15 g (33%); $^1$H NMR (400 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ 0.26 (s, $SiCH_3$); $^{13}$C NMR (100.6 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ -0.06 (s, $SiCH_3$); $^{119}$Sn NMR (149.3 MHz, $C_6D_6$, 25ºC, $Me_4Sn$): $\delta$ 782 (s); MS (EI, 174°C): *m/z* 824 [$M^+$]; IR (nujol): 1301 (m), 852 (s), 749 (m), 722 (m), 518 (m) cm$^{-1}$; elemental analysis calculated (%) for $C_{12}H_{36}N_4Si_4Sn_4$: C 17.49, H 4.41; found: C 17.51, H 4.42.

Crystal data for **13**. $C_{12}H_{36}N_4Si_4Sn_4$: $M_r$ = 869.64g cm$^{-3}$, crystal dimensions 0.221 x 0.204 x 0.102 mm, monoclinic, space group *C*2/m, $a$ = 26.05(2), $b$ = 12.066(9), $c$ = 10.933(8) Å, α = 90, $\beta$ = 110.176º; $V$ = 3225(4) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 1.791 g cm$^{-3}$, Siemens SMART CCD diffractometer, 1.67 ≤ $\theta$ ≤ 28.77˚, $Mo_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å), $\omega$ scans, $T$ = 193(2) K; of 10,430 measured reflections, 4,037 were independent and 2,894 observed with $I > 2\sigma(I)$, -28 ≤ $h$ ≤ 33, -15 ≤ $k$ ≤ 14, -14 ≤ $l$ ≤ 9; $R_1$ = 0.0349, $wR_2$ = 0.0711, GOF = 1.053 for 141 parameters, $\Delta\rho_{max}$ = 0.981 eÅ$^{-3}$. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-97), Lorentz polarization corrections and absorption correction (SADABS) were applied, $\mu$ = 3.220 mm$^{-1}$, min./max. transmission 0.7348/0.5364.

*Synthesis of [Ge($\mu_3$-NSiMe$_3$)]$_4$* (**14**): Compound **14** was prepared in an analogous fashion to compound **13** using [(Me$_3$Sn)(Me$_3$Si)NLi•(Et$_2$O)]$_2$ (0.80 g, 1.20 mmol) and GeCl$_2$ (0.34g, 2.41 mmol). Pale yellow crystals were grown from $CH_2Cl_2$ at –80°C over a two-day period. Yield: 0.11 g (29%); Pale yellow crystals decomposed at 190°C; $^1$H NMR (400 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ 0.312 (s, SiCH$_3$); $^{13}$C NMR (100.6 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ -1.465 (s, SiCH$_3$); elemental analysis calculated (%) for $C_{12}H_{36}N_4Ge_4Si_4$: C 22.55, H 5.68, N 8.76, found: C 23.56, H 5.24, N 9.10.

Crystal data for **14**. $C_{15.5}H_{40}N_4Ge_4Si_4$: $M_r$ = 685.23 g cm$^{-3}$, crystal dimensions 0.56 x 0.20 x 0.17 mm, monoclinic, space group *C*2/*c*, $a$ = 25.748(5), $b$ = 11.878(2), $c$ = 21.478(4) Å, α = 90, $\beta$ = 110.690º; $V$ = 6145(2) Å$^3$, $Z$ = 8, $\rho_{calcd}$ = 1.481 g cm$^{-3}$, Siemens SMART CCD diffractometer, $1.69 \leq \theta \leq 28.70^{\circ}$, $Mo_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å), $\omega$ scans, $T$ = 193(2) K; of 18,078 measured reflections, 7,251 were independent and 5,531 observed with $I > 2\sigma(I)$, $-29 \leq h \leq 33$, $-14 \leq k \leq 15$, $-28 \leq l \leq 12$; $R_1$ = 0.0506, $wR_2$ = 0.1330, GOF = 1.057 for 269 parameters, $\Delta\rho_{max}$ = 1.412 eÅ$^{-3}$. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-97), Lorentz polarization corrections and absorption correction (SADABS) were applied, $\mu$ = 4.041 mm$^{-1}$, min./max. transmission 0.5466/0.2102.

*Synthesis of [Pb($\mu_3$-NSiMe$_3$)]$_4$* (**15**): Compound **15** was prepared in an analogous fashion to compound **13** using [(Me$_3$Sn)(Me$_3$Si)NLi•(Et$_2$O)]$_2$ (0.75 g, 1.13 mmol) and PbCl$_2$ (0.63g, 2.26 mmol). Yellow crystals were grown from $CH_2Cl_2$ at –80°C over a two-day period. Yield: 0.25 g (38%); Yellow crystals decomposed at 225°C; $^1$H NMR (400 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ 0.027 (s, SiCH$_3$); $^{13}$C NMR (100.6 MHz, $C_6D_6$, 25ºC, TMS):

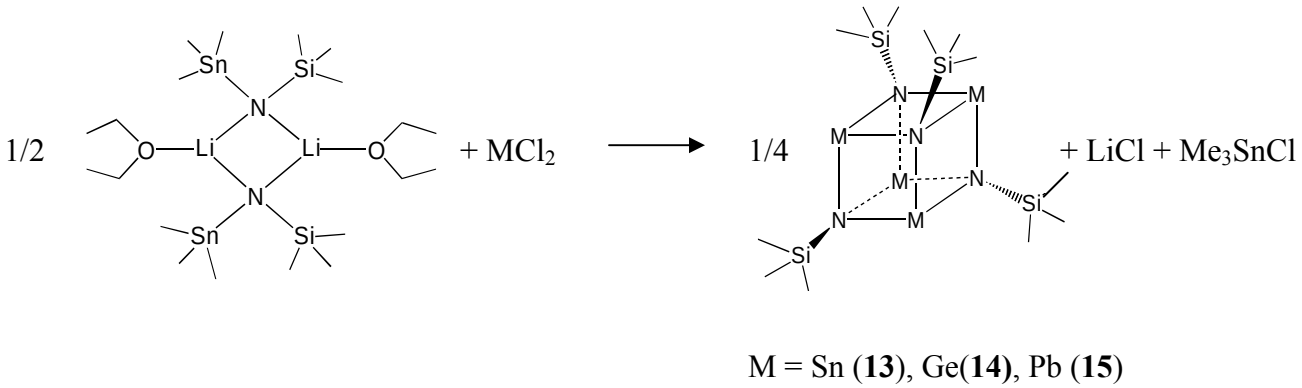
$\delta$ -0.389 (s, $SiCH_3$); MS (EI, 274°C): *m/z* 1178 [$M^+$]; IR (nujol): 1255 (m), 1242 (m), 864 (m), 826 (s), 741 (m), 523 (m) $cm^{-1}$; elemental analysis calculated (%) for $C_{12}H_{36}N_4Pb_4Si_4$: C 12.24, H 3.08, N 4.76, found: C 12.19, H 3.09, N 4.89.

Crystal data for **15**. $C_{12}H_{36}N_4Pb_4Si_4$: $M_r$ = 1177.57 g $cm^{-3}$, crystal dimensions 0.459 x 0.408 x 0.170 mm, trigonal, space group *R*-3, $a$ = 10.7447(8), $c$ = 47.935(7) Å, α = 90, $\gamma$ = 120º; $V$ = 4792.6(9) $Å^3$, $Z$ = 6, $\rho_{calcd}$ = 2.448 g $cm^{-3}$, Siemens SMART CCD diffractometer, $2.23 \leq \theta \leq 28.74^{\circ}$, $Mo_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å), $\omega$ scans, $T$ = 193(2) K; of 8,240 measured reflections, 2,473 were independent and 2,127 observed with $I > 2\sigma(I)$, $-14 \leq h \leq 11$, $-12 \leq k \leq 14$, $-54 \leq l \leq 63$; $R_1$ = 0.0507, $wR_2$ = 0.1426, GOF = 1.082 for 82 parameters, $\Delta\rho_{max}$ = 4.103 $eÅ^{-3}$. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-97), Lorentz polarization corrections and absorption correction (SADABS) were applied, $\mu$ = 21.167 $mm^{-1}$, min./max. transmission 0.1234/0.0368.

**Results and Discussion**

*Synthesis*

Compounds **13**-**15** were prepared analogously by reacting the appropriate divalent metal chloride with 0.5 equivalents of compound **2** (see Scheme 5.1). The reaction mixtures were stirred overnight at room temperature and then filtered to remove LiCl. The solvent was then removed, the solid product residues extracted with 15 mL of $CH_2Cl_2$, and crystals of each compound grown over a two-day period at –80ºC.




**Scheme 5.1**. Synthesis of compounds **13-15.**

*Characterization*

Crystals of compounds **13-15** were each analyzed by a single crystal X-ray diffraction experiment. The results are shown in Figures 5.1-5.3.

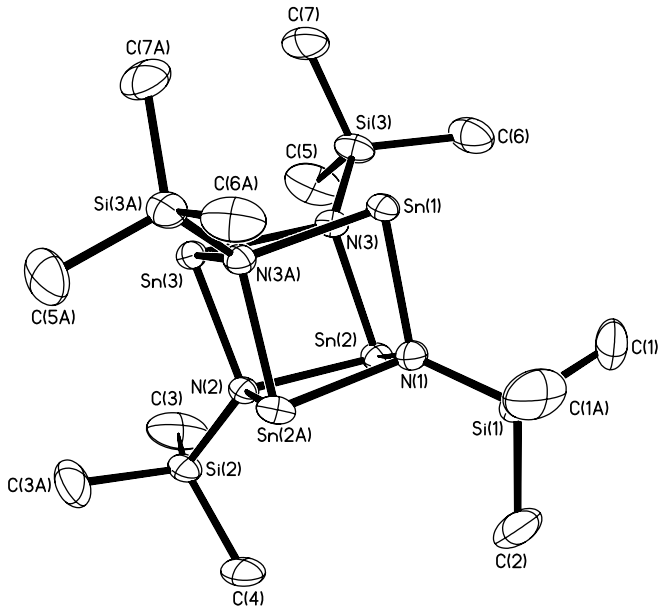



**Figure 5.1**. ORTEP plot representation (30% probability) with numbering scheme for compound **13**. Hydrogen atoms have been omitted for clarity.

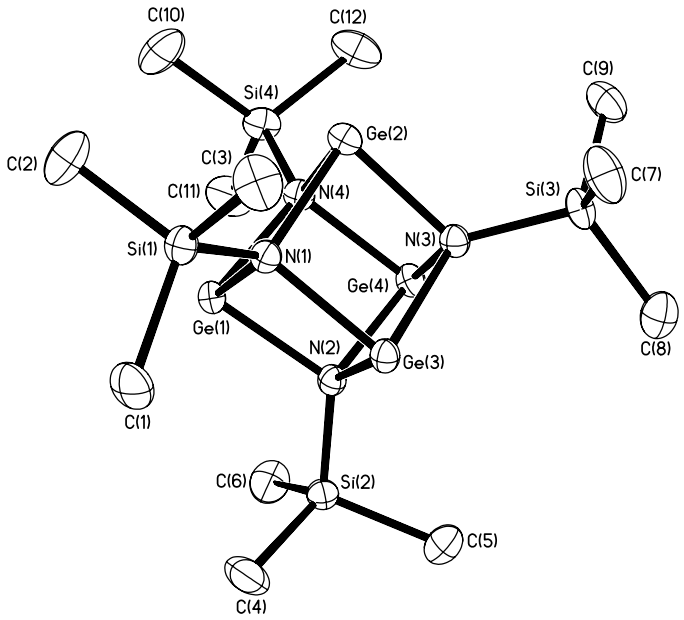



**Figure 5.2**. ORTEP plot representation (30% probability) with numbering scheme for compound **14**. Hydrogen atoms have been omitted for clarity.

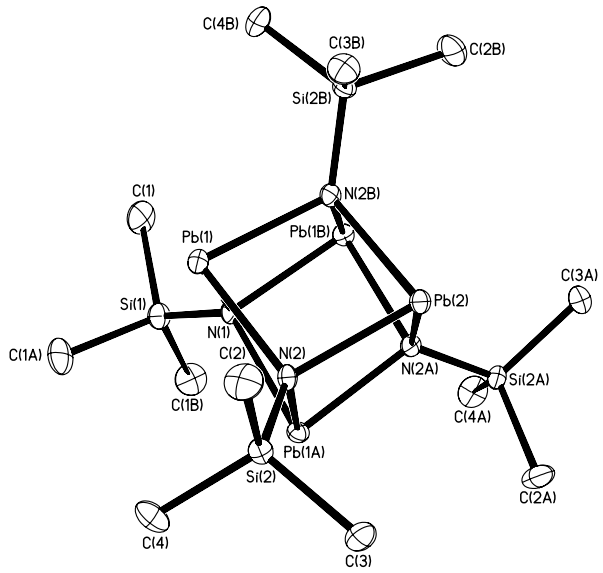



**Figure 5.3**. ORTEP plot representation (30% probability) with numbering scheme for compound **15**. Hydrogen atoms have been omitted for clarity.

All three complexes exist as tetramers in the solid state, with the trimethylsilyl imide units each bridging three divalent metal centers. A summary of the principal interatomic distances and angles for compounds **13**-**15** is provided in Table 5.1, and a complete list of all distances and angles can be found in Tables A.48, A.52, and A.56, respectively.

**Table 5.1**. Selected average interatomic distances (Å) and angles (degrees) for compounds **13**-**15.**

| (**13**) | distance/angle | (**14**) | distance/angle | (**15**) | distance/angle |
|---|---|---|---|---|---|
| Si-N | 1.733(5) | Si-N | 1.742(3) | Si-N | 1.704(11) |
| Sn-N | 2.203(4) | Ge-N | 2.013(3) | Pb-N | 2.301(7) |
| Sn-N-Sn | 97.26(14) | Ge-N-Ge | 96.65(12) | Pb-N-Pb | 97.4(3) |
| N-Sn-N | 82.27(15) | N-GeN | 84.06(6) | N-Pb-N | 81.8(3) |

Although the synthesis of compound **13** (via the reaction of **2** with $SnCl_2$) differs from the route employed by Veith, *et al*., who reacted the cyclic diazastannylene, $Sn(^tBuN)_2SiMe_2$, with the primary amine, $Me_2SiNH_2$,[4] the results of single crystal X-ray diffraction studies are in both cases analogous.

Conversely, the incorporation of the trimethylsilyl moiety into germanium- or lead-nitrogen cubanes has to our knowledge not been reported to date. However, the configuration of the central $M_4N_4$ skeleton does not differ drastically from other Group 14-nitrogen cubane species described formerly. The $M_4N_4$ core for both **14** and **15** exhibits a distortion from a perfect cube, as evidenced by the average angles of 84.06º (N-Ge-N) and 96.65º (Ge-N-Ge) in **14,** as well as the average angles of 81.8º (N-Pb-N)

and 97.40º (Pb-N-Pb) in **15**. This type of distortion is common for similar Group 14-nitrogen cubanes. Comparison to compound **13** (average N-Sn-N = 83.12º and average Sn-N-Sn = 96.52º) indicates an increasing trend of distortion from perfect cube geometry from germanium to lead. This can be attributed to the decrease in sp-hybridization in the heavier tin and lead atoms. The average Ge-N and Pb-N interatomic distances of 2.013 Å in **14** and 2.304 Å in **15** are comparable to those found in previous reports: $[GeN(C_6H_6)]_4$, 2.019 Å;[5] $[PbN(C_6H_{12})]_4$, 2.303 Å;[6] and $[PbN(2,6\text{-}i\text{-}Pr_2C_6H_3)]_4$, 2.337 Å[7]. The distorted tetrahedral geometry about the silicon atoms in **14** and **15**, with average Si-N interatomic distances of 1.742 and 1.704 Å, respectively, is in agreement with previous structures containing the trimethylsilyl moiety in a similar chemical environment: $(Me_3C)Al_2Li_2[\mu_3\text{-}N(SiMe_3)]_4$, $Si\text{-}N_{avg}$ = 1.691 Å;[8] $[MeGa(\mu_3\text{-}NSiMe_3)]_4$, $Si\text{-}N_{avg}$ = 1.727 Å;[9] $[MeIn(\mu_3\text{-}NSiMe_3)]_2\cdot[Li(Me_3Si)N\text{-}NH^tBu]_2$, $Si\text{-}N_{avg}$ = 1.743 Å.[10]

Since it is ultimately desired to utilize this class of compounds as MOCVD precursors, it was of utmost importance to determine whether these high molecular weight compounds possess sufficient volatility and vapor phase stability. The results of the thermogravimetric analysis (TGA) of compound **15 (**Figure 5.4) indicate that complexes possessing this tetranuclear geometry exhibit sufficient volatility and vapor phase integrity for potential employment as MOCVD precursors.

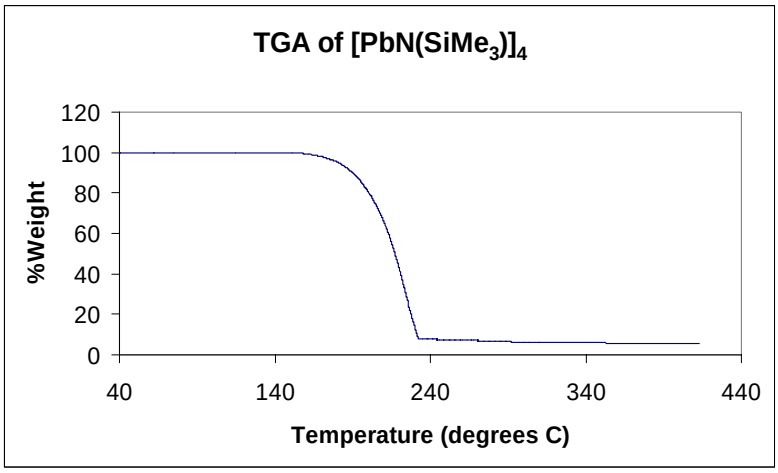



**Figure 5.4**. TGA plot of percent weight vs. temperature for compound **15**.

## Conclusion

Compound **13**, previously synthesized and characterized by Veith, *et al*., was prepared using a method that employed the heteroleptic stannylamide, $[(Me_3Sn)(Me_3Si)NLi{\bullet}Et_2O]_2$ (**2**) as a starting material. This synthetic route was successfully extended to the congeners possessing germanium and lead. Compounds **14** and **15** are rare examples of Ge- and Pb-nitrogen heterocubanes and represent the first report of either class of compounds that contain the trimethylsilyl moiety. These results demonstrate the success of the molecular design strategy aimed at changing the identity of the endo-cube dicationic metal and indicate that the use of other lithiated stannylamides, such as $[(Me_3Sn)_2NLi{\bullet}Et_2O]_2$ (**1**) and $[(Me_3Sn)(Me_3Ge)NLi{\bullet}Et_2O]_2$ (**3**), may provide access to additional series of Group 14-nitrogen hetercubanes.

SECTION B: MOLECULAR DESIGN OF GROUP 14-NITROGEN HETEROCUBANES - MODIFICATION OF THE EXO-CUBE SUBSTITUENT: $[Sn(\mu_3\text{-}NEMe_3)]_4$ (E = Ge, Sn)

## Introduction

Chapter 5 – Part A demonstrates the modification of the endo-cube dicationic metal by reacting the appropriate metal dichloride with the heteroleptic stannylamide, $[(Me_3Sn)(Me_3Si)NLi{\bullet}Et_2O]_2$ (**2**). This sub-chapter aims to arrive at a synthetic route that can exhibit control over the identity of the exo-cube subsituent. Thus, the synthesis and characterization of the tin-nitrogen heterocubanes, $[Sn(\mu_3\text{-}NGeMe_3)]_4$ (**16**) and $[Sn(\mu_3\text{-}NSnMe_3)]_4$ (**17**) are described herein.

## Experimental

All manipulations were carried out in a dry atmosphere glovebox or by standard Schlenk techniques. All solvents were dried over Na° metal or $P_2O_5$ ($CH_2Cl_2$) and were freshly distilled under an inert atmosphere prior to use. $SnCl_2$ was purchased from Alfa Aesar and used without further purification. $[(Me_3Sn)_2NLi{\bullet}(THF)]_2$ and $[(Me_3Sn)(Me_3Ge)NLi{\bullet}(Et_2O)]_2$ were prepared as described in Chapter 2. All NMR experiments were performed on a Bruker 400 MHz Spectrometer at 300K using $C_6D_6$ solvent that was distilled over $CaH_2$ and stored under argon. $^{1}H$ and $^{13}C$ spectra were referenced to TMS. $^{119}Sn$ spectra were externally referenced to $Me_4Sn$. Elemental analyses were performed in triplicate on a Perkin Elmer Series II CHNS/O Analyzer

2400, FT-IR measurements were performed on a Bruker Equinox 55 Spectrometer, mass spectrometry analyses were done on a VG Instruments 70SE (Electron Impact; 70eV), and UV/VIS measurements were performed on a Perkin Elmer UV/VIS/NIR Lambda 19 Spectrometer. All TGA experiments were performed on a Perkin Elmer 7/DX thermal analyser interfaced to a Perkin Elmer Thermal Analysis Controller (TAC). The instrument is housed in a dry atmosphere glovebox. Argon was used as the purge gas and all %weight vs. temperature profiles were done at a 10ºC/min. temperature ramp under ambient pressure.

*Synthesis of [Sn($\mu_3$-NGeMe$_3$)]$_4$* (**16**): Compound **16** was prepared in an analogous fashion to compound **13** using [(Me$_3$Sn)(Me$_3$Ge)NLi•(Et$_2$O)]$_2$ (0.50 g, 0.66 mmol) and $SnCl_2$ (0.25 g, 1.33 mmol). Yellow crystals were grown from $CH_2Cl_2$ at –80°C over a two-day period. Yield: 0.07 g (21%); Yellow crystals decomposed at 250°C; $^1$H NMR (400 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ 0.45 (s, $GeCH_3$); $^{13}$C NMR (100.6 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ 0.21 (s, $GeCH_3$); $^{119}$Sn NMR (149.3 MHz, $C_6D_6$, 25ºC, $Me_4Sn$): $\delta$ 954 (s); MS (EI, 270°C): *m/z* 1002 [$M^+$]; IR (nujol): 1075 (m), 818 (m), 725 (m), 599(s), 563 (m), 515 (m) cm$^{-1}$; elemental analysis calculated (%) for $C_{12}H_{36}N_4Sn_4Ge_4$: C 14.39, H 3.62, N 5.59, found: C 14.41, H 3.22, N 5.71.

Crystal data for **16**. $C_{12}H_{36}N_4Sn_4Ge_4$: $M_r$ = 1033.57 g cm$^{-3}$, crystal dimensions 0.19 x 0.09 x 0.07 mm, monoclinic, space group *C*2/*c*, *a* = 12.520(4), *b* = 17.891(5), *c* = 15.642(5) Å, α = 90, $\beta$ = 107.536º; *V* = 3341.1(17) Å$^3$, *Z* = 4, $\rho_{calcd}$ = 2.055 g cm$^{-3}$, Siemens SMART CCD diffractometer, $2.05 \leq \theta \leq 28.75^\circ$, $Mo_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å), $\omega$ scans, *T* = 193(2) K; of 10,311 measured reflections, 3,989 were independent and

1,908 observed with $I > 2\sigma(I)$, $-8 \leq h \leq 16$, $-18 \leq k \leq 23$, $-21 \leq l \leq 19$; $R_1 = 0.0865$, $wR_2 = 0.2208$, GOF = 0.975 for 130 parameters, $\Delta\rho_{max} = 4.388$ eÅ$^{-3}$. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-97), Lorentz polarization corrections and absorption correction (SADABS) were applied, $\mu = 6.497$ mm$^{-1}$, min./max. transmission 0.6664/0.3763.

*Synthesis of [Sn($\mu_3$-NSnMe$_3$)]$_4$* (**17**): Compound **17** was prepared in an analogous fashion to compound **13** using [(Me$_3$Sn)$_2$NLi•(THF)]$_2$ (0.50 g, 0.59 mmol) and SnCl$_2$ (0.22 g, 1.19 mmol). Orange crystals were grown from $CH_2Cl_2$ at –80°C over a two-day period. Yield: 0.18 g (51%); Orange crystals decomposed at 210°C; $^1$H NMR (400 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ 0.29 (s, SnCH$_3$); $^{13}$C NMR (100.6 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ 1.36 (s, SnCH$_3$); $^{119}$Sn NMR (149.3 MHz, $C_6D_6$, 25ºC, Me$_4$Sn): $\delta$ –40.4 (s, SnMe$_3$), 797.3 (s, Sn($u_3$-N)); MS (EI, 273°C): *m/z* 1188 [M$^+$]; IR (nujol): 1181 (w), 1033 (m), 721 (m), 663 (m), 529 (w) cm$^{-1}$; elemental analysis calculated (%) for $C_{12}H_{36}N_4Sn_8$: C 12.15, H 3.06, N 4.72, found: C 11.96, H 2.78, N 3.96.

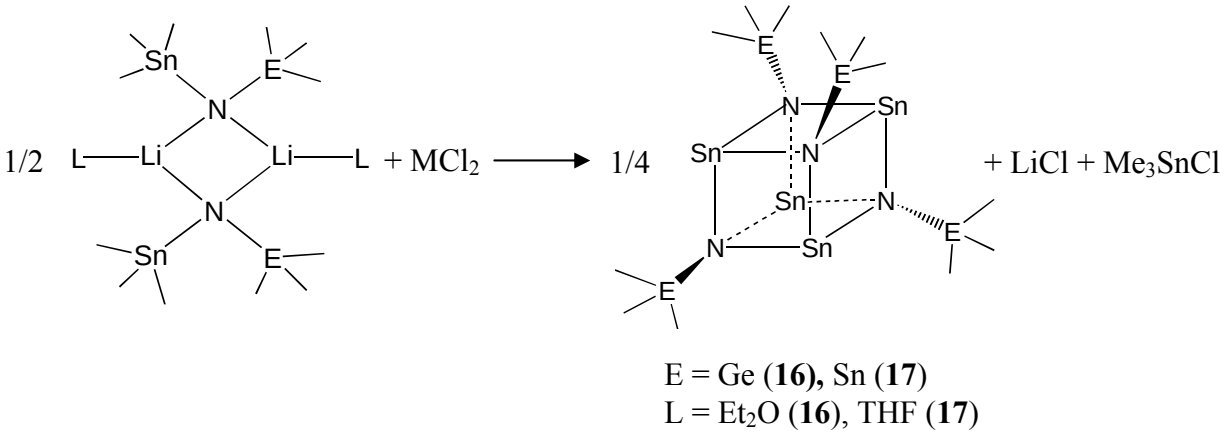
Crystal data for **17**. $C_{12}H_{36}N_4Sn_8$: $M_r = 1185.97$ g cm$^{-3}$, crystal dimensions 0.14 x 0.10 x 0.10 mm, cubic, space group *I*-43*m*, $a = 11.6106(14)$ Å, $\alpha = 90$º; $V = 1565.2(3)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 2.516$ g cm$^{-3}$, Siemens SMART CCD diffractometer, $2.48 \leq \theta \leq 28.69$°, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\omega$ scans, $T = 193(2)$ K; of 4,478 measured reflections, 405 were independent and 394 observed with $I > 2\sigma(I)$, $-15 \leq h \leq 15$, $-15 \leq k \leq 15$, $-8 \leq l \leq 15$; $R_1 = 0.0214$, $wR_2 = 0.0474$, GOF = 1.226 for 18 parameters, $\Delta\rho_{max} = 0.915$ eÅ$^{-3}$. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-97), Lorentz polarization corrections and absorption

correction (SADABS) were applied, $\mu$ = 6.276 $mm^{-1}$, min./max. transmission 0.5669/0.4823.

**Results and Discussion**

*Synthesis*

Compounds **16** and **17** were prepared analogously by reacting the appropriate divalent metal chloride with 0.5 equivalents of compound **2** (see Scheme 5.2). The reaction mixtures were stirred overnight at room temperature and LiCl was filtered off. The solvent was then removed, the solid product residues extracted into about 15 mL of $CH_2Cl_2$, and crystals of each compound were grown over a two-day period at –80ºC.




**Scheme 5.2**. Synthesis of compounds **16-17.**

*Characterization*

Crystals of compounds **16** and **17** were each analyzed by a single crystal X-ray diffraction experiment. The results are shown in Figures 5.5 and 5.6.

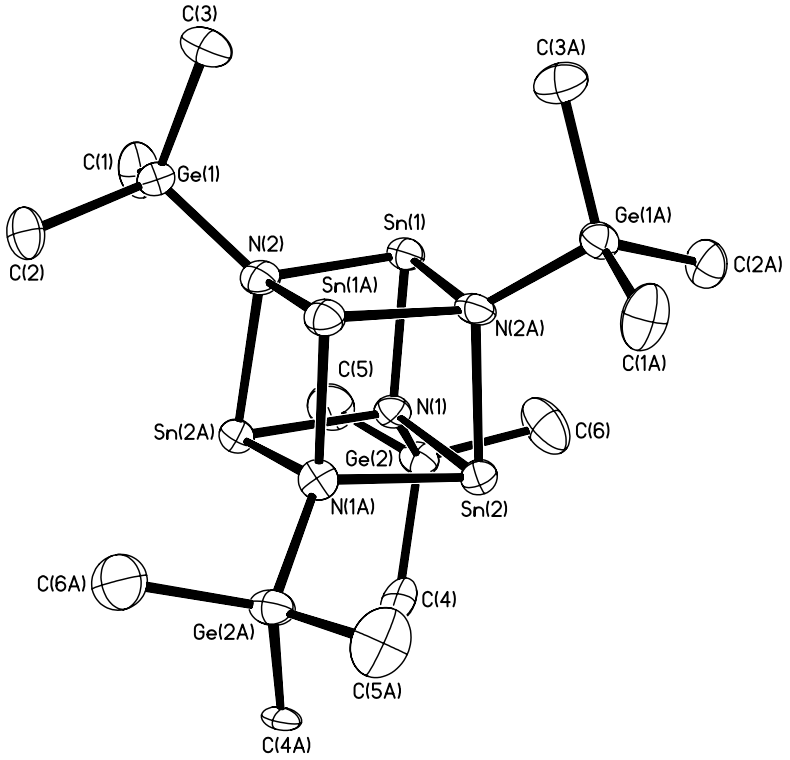



**Figure 5.5**. ORTEP plot representation (30% probability) with numbering scheme for compound **16**. Hydrogen atoms have been omitted for clarity.

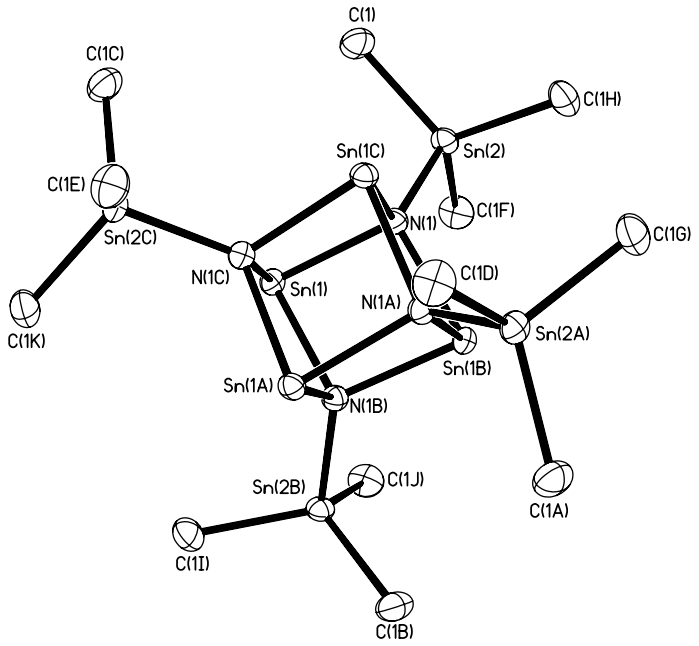



**Figure 5.6**. ORTEP plot representation (30% probability) with numbering scheme for compound **17**. Hydrogen atoms have been omitted for clarity.

Both complexes exist as tetramers in the solid state, with the trimethylstannyl and trimethylgermyl imide units each bridging three divalent metal centers. A summary of the principal interatomic distances and angles for compounds **16** and **17** is provided in Table 5.2, and a complete list of all distances and angles can be found in Tables A.60 and A.64, respectively.

**Table 5.2**. Selected average interatomic distances (Å) and angles (degrees) for compounds **16** and **17.**

| (**16**) | distance/angle | (**17**) | distance/angle |
|---|---|---|---|
| Ge-N | 1.860(12) | Sn-N | 2.043(7) |
| Sn-N (endo-cube) | 2.207(11) | Sn-N (endo-cube) | 2.196(3) |
| Sn-N-Sn | 97.2(4) | Sn-N-Sn | 96.5(2) |
| N-Sn-N | 82.27(4) | N-Sn-N | 83.1(2) |

The simultaneous interaction of nitrogen with Sn(II) and Ge(IV) metal centers observed in **16** is to our knowledge unique. In addition, this compound is the first Group 14-nitrogen heterocubane possessing exo-cube germanium. However, the configuration of the central $Sn_4N_4$ skeleton does not differ drastically from other tin-nitrogen cubane species previously reported in the literature. The $Sn_4N_4$ core exhibits a distortion from a perfect cube, as evidenced by the average N-Sn(1)-N angle of 82.27(4)º and the average Sn-N-Sn angle of 97.2(4)º. This distortion is commonplace in such Group 14-nitrogen cubanes, and was also observed in compounds **13**-**15**. The average Ge-N interatomic

distance [1.860(12) Å] is in agreement with previously reported values [(Li[N($GeMe_3$)$_2$])$_3$, Ge-$N_{avg}$ = 1.837 Å].[11]

The occurrence of the nitrogen-bridged Sn(II) and Sn(IV) centers observed in **17** is also believed to be unprecedented and the exo-cube trimethyltin moiety represents the heaviest exo-cube subsituent in a Group 14-nitrogen cubane to date. The $Sn_4N_4$ core in **17** also exhibits distortion from a perfect cube, as evidenced by the average N-Sn(1)-N angle of 83.1(2)º and the average Sn-N-Sn angle of 96.5(2)º. This distortion is analogous to that observed in compounds **1**3-**16**. The geometry about the tin(IV) atoms is distorted tetrahedral and the average Sn-N interatomic distance of 2.043(7) Å is in agreement with tin(IV)-nitrogen distances previously reported: SnBr[N($SiMe_3$)$_2$]$_3$, 2.056(7) Å;[12] Sn($CH_3$)(NRAr)$_3$, (R = C($CD_3$)$_2$$CH_3$, Ar = 3,5-$C_6H_3Me_2$), 2.044(4)Å[13] and Sn($NCPh_2$)$_4$, 2.068(37) Å).[14] The average Sn(II)-N interatomic distances in both **16** and **17** are similar to values found for other tin-nitrogen cubanes: [Sn($\mu_3$-$NSiMe_3$)]$_4$, 2.196(4) Å;[4] [Sn($\mu_3$-N{4-$MeOC_6H_6$})]$_4$, 2.205(3) Å[15] and [Sn($\mu_3$-N{2,6-$^i$$Pr_2C_6H_3$})]$_4$, 2.227(8) Å.[16]

The tin-nitrogen heterocubanes, **13**, **16**, and **17** were also characterized by multinuclear NMR techniques. Specifically, the $^{119}$Sn NMR of these compounds aids in verifying the oxidation state of the tin(II) atoms located in the endo-cube position, and in the case of compound **17**, the oxidation state of the exo-cube trimethyl tin moiety. The positions of the $^{119}$Sn resonances for these compounds are summarized in Table 5.3. The endo-cube tin resonances for **13**, **16**, and **17** do not show any discernable trend, but do fall in the predicted range for tin(II) cations. The exo-cube tin resonance found in **17** is observed at higher field, expected for tin(IV) nuclei (see Figure 5.7).

**Table 5.3**. $^{119}$Sn NMR resonances observed for compounds **13**, **16**, and **17.**

| (**13**) | Resonance (ppm) | (**16**) | Resonance (ppm) | (**17**) | Resonance (ppm) |
|---|---|---|---|---|---|
| Endo-cube Sn(II) | 782 | Endo-cube Sn(II) | 954 | Endo-cube Sn(II) | 797 |
| Exo-cube Sn(IV) | - | - | - | - | -40 |

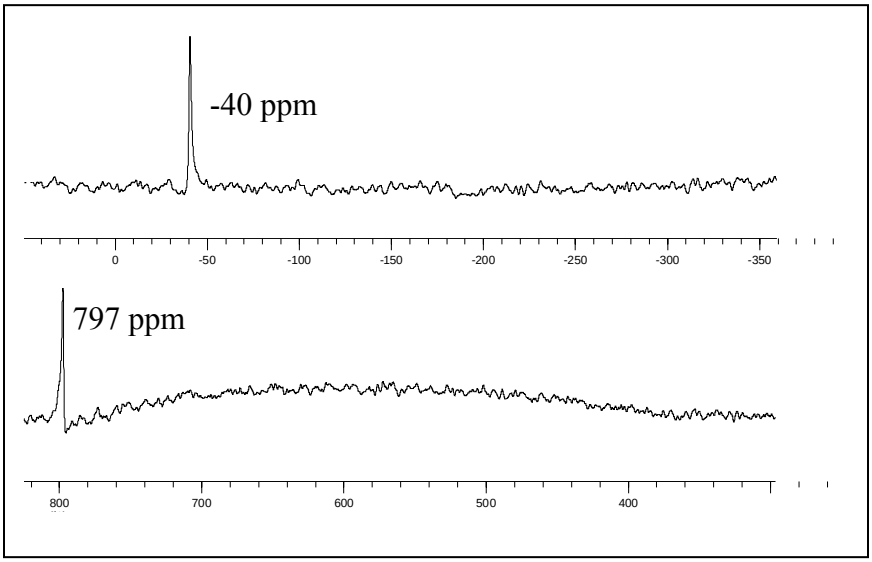



**Figure 5.7**. $^{119}$Sn NMR spectrum of compound **17** (chemical shift scale in ppm).

The volatility of compound **17** was determined by TGA. The cubane species is volatile below 250ºC, but appears to decompose at higher temperatures. The TGA plot of percent weight versus temperature is graphically depicted in Figure 5.8.

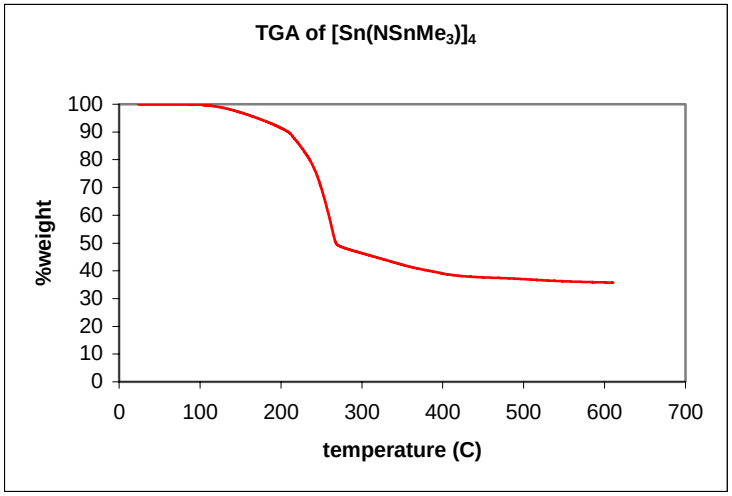



**Figure 5.8**. TGA plot of percent weight vs. temperature for compound **17**.

## Conclusion

Since the molecular design of the endo-cube metal in Group 14-nitrogen heterocubanes was achieved in Chapter 5 – Part A, it was of interest to determine if the identity of the exo-cube substituent could also be controlled. Thus, this chapter describes the synthesis and characterization of the tin-nitrogen heterocubanes possessing exo-cube germanium and exo-cube tin, $[Sn(\mu_3\text{-}NGeMe_3)]_4$ (**16**) and $[Sn(\mu_3\text{-}NSnMe_3)]_4$ (**17**). The preparation of these compounds demonstrates that not only the endo-cube metal, but also the exo-cube heavy-atom substituent can be modified. In addition, compounds **16**-**17**, as well as

compound **13** are amenable to characterization via $^{119}$Sn NMR and provide spectroscopic information on tin nuclei that are found in unusual coordination environments. The results reported here are encouraging in the respect that additional Group 14-nitrogen heterocubane species may be successfully synthesized and that the molecular design of this class of compounds may ultimately lead to precursors for the MOCVD of ZTT.

## SECTION C: MOLECULAR DESIGN OF GROUP 14-NITROGEN HETEROCUBANES - MODIFICATION OF BOTH THE EXO- AND ENDO-CUBE SUBSTITUENT: $[M(\mu_3\text{-}NGeMe_3)]_4$ (M = Ge, Pb)

### Introduction

The first two sub-chapters described the synthesis and characterization of a variety of Group 14-nitrogen heterocubanes. Chapter 5 – Part A demonstrated that the endo-cube metal could be altered by changing the metal dichloride used in the synthetic workup. Chapter 5 – Part B established that the exo-cube substituent could be modified by using a different lithiated stannylamine in the course of the synthesis. This chapter describes the procedures used to obtain analogous heterocubane species possessing both modified endo-cube dications and exo-cube substituents. Thus, the synthesis and characterization of $[Ge(\mu_3\text{-}NGeMe_3)]_4$ (**18**) and $[Pb(\mu_3\text{-}NGeMe_3)]_4$ (**19**) is described herein.

### Experimental

All manipulations were carried out in a dry atmosphere glovebox or by standard Schlenk techniques. All solvents were dried over Na$^o$ metal or $P_2O_5$ ($CH_2Cl_2$) and were freshly distilled under an inert atmosphere prior to use. $SnCl_2$ and $PbCl_2$ reagents were purchased from Alfa Aesar and used without further purification. $[(Me_3Sn)_2NLi\bullet(THF)]_2$, $[(Me_3Sn)(Me_3Si)NLi\bullet(Et_2O)]_2$, and $[(Me_3Sn)(Me_3Ge)NLi\bullet(Et_2O)]_2$ were prepared as described in Chapter 2. $GeCl_2\cdot$(dioxane) was prepared according to literature procedures.[3] All NMR experiments were performed on a Bruker 400 MHz Spectrometer at 300K using $C_6D_6$ solvent that was distilled over $CaH_2$ and stored under argon. $^1H$, $^{13}C$,

and $^{29}$Si spectra were referenced to TMS. $^{119}$Sn and $^{7}$Li spectra were externally referenced to $Me_4Sn$ and LiBr respectively. Elemental analyses were performed in triplicate on a Perkin Elmer Series II CHNS/O Analyzer 2400, FT-IR measurements were performed on a Bruker Equinox 55 Spectrometer, mass spectrometry analyses were done on a VG Instruments 70SE (Electron Impact; 70eV), and UV/VIS measurements were performed on a Perkin Elmer UV/VIS/NIR Lambda 19 Spectrometer. All TGA experiments were performed on a Perkin Elmer 7/DX thermal analyser interfaced to a Perkin Elmer Thermal Analysis Controller (TAC). The instrument is housed in a dry atmosphere glovebox. Argon was used as the purge gas and all %weight vs. temperature profiles were done at a 10ºC/min. temperature ramp under ambient pressure.

*Synthesis of [Ge($\mu_3$-NGeMe$_3$)]$_4$* (**18**): Compound **18** was prepared in an analogous fashion to compound **13** using [(Me$_3$Sn)(Me$_3$Ge)NLi•(Et$_2$O)]$_2$ (0.60 g, 0.80 mmol) and $GeCl_2$ (0.23 g, 1.60 mmol). Pale yellow crystals were grown from $CH_2Cl_2$ at –80°C over a two-day period. Yield: 0.05 g (15%); Pale yellow crystals decomposed at 265°C; $^1$H NMR (400 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ 0.50 (s, $GeCH_3$); $^{13}$C NMR (100.6 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ –1.14 (s, $GeCH_3$); MS (EI, 274°C): *m/z* 820 [$M^+$]; IR (nujol): 1261 (m), 1231 (m), 1015 (s), 824 (m), 735 (m), 603 (m), 558 (m) cm$^{-1}$; elemental analysis calculated (%) for $C_{12}H_{36}N_4Ge_8$: C 17.62, H 4.44, N 6.86, found: C 17.74, H 4.34, N 7.34.

Crystal data for **18**. $C_{12}H_{36}N_4Ge_8$: $M_r$ = 817.17 g cm$^{-3}$, crystal dimensions 0.17 x 0.14 x 0.10 mm, cubic, space group *I*-43*m*, *a* = 11.2872(10) Å, $\beta$ = 90º; *V* = 1438.0(2) Å$^3$, *Z* = 2, $\rho_{calcd}$ = 1.887 g cm$^{-3}$, Siemens SMART CCD diffractometer, 2.55 ≤ $\theta$ ≤ 28.79˚, $Mo_{K\alpha}$

radiation ($\lambda$ = 0.71073 Å), $\omega$ scans, $T$ = 193(2) K; of 4,569 measured reflections, 369 were independent and 329 observed with $I > 2\sigma(I)$, $-14 \leq h \leq 15$, $-12 \leq k \leq 15$, $-15 \leq l \leq 14$; $R_1$ = 0.0339, $wR_2$ = 0.0757, GOF = 1.047 for 18 parameters, $\Delta\rho_{max}$ = 0.785 eÅ$^{-3}$. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-97), Lorentz polarization corrections and absorption correction (SADABS) were applied, $\mu$ = 8.245 mm$^{-1}$, min./max. transmission 0.4868/0.3346.

*Synthesis of [Pb($\mu_3$-NGeMe$_3$)]$_4$* (**19**): Compound **19** was prepared in an analogous fashion to compound **13** using [(Me$_3$Sn)(Me$_3$Ge)NLi•(Et$_2$O)]$_2$ (0.50 g, 0.66 mmol) and PbCl$_2$ (0.37 g, 1.33 mmol). Yellow crystals were grown from CH$_2$Cl$_2$ at –80°C over a two-day period. Yield: 0.25 g (55%); Yellow crystals decomposed at 265°C; $^1$H NMR (400 MHz, C$_6$D$_6$, 25ºC, TMS): $\delta$ 0.19 (s, GeCH$_3$); $^{13}$C NMR (100.6 MHz, C$_6$D$_6$, 25ºC, TMS): $\delta$ –1.02 (s, GeCH$_3$); MS (EI, 42°C): *m/z* 1356 [M$^+$]; IR (nujol): 1228 (m), 812 (m), 719 (m), 589(m), 531 (w) cm$^{-1}$; elemental analysis calculated (%) for C$_{12}$H$_{36}$N$_4$Pb$_4$Ge$_4$: C 10.63, H 2.68, N 4.13, found: C 10.57, H 2.61, N 4.22.

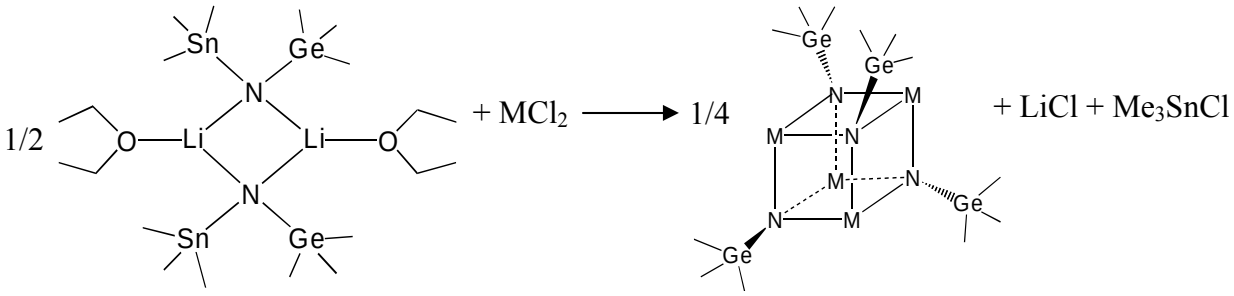
Crystal data for **19**. $M_r$ = 2674.85 g cm$^{-3}$, crystal dimensions 0.374 x 0.136 x 0.119 mm, cubic, space group *P*-43*n*, $a$ = 18.2282(14) Å, α = 90º; $V$ = 6056.6(8) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 2.933 g cm$^{-3}$, Siemens SMART CCD diffractometer, $1.58 \leq \theta \leq 28.68^\circ$, Mo$_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å), $\omega$ scans, $T$ = 193(2) K; of 36,464 measured reflections, 2,561 were independent and 1,359 observed with $I > 2\sigma(I)$, $-21 \leq h \leq 23$, $-23 \leq k \leq 24$, $-14 \leq l \leq 23$; $R_1$ = 0.0579, $wR_2$ = 0.1416, GOF = 0.974 for 73 parameters, $\Delta\rho_{max}$ = 2.855 eÅ$^{-3}$. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-

squares procedures (SHELXL-97), Lorentz polarization corrections and absorption correction (SADABS) were applied, $\mu$ = 26.067 $mm^{-1}$, min./max. transmission 0.5466/0.2102.

**Results and Discussion**

*Synthesis*

Compounds **18** and **19** were prepared analogously by reacting the appropriate divalent metal chloride with 0.5 equivalents of compound **3** (see Scheme 5.3). The reaction mixtures were stirred overnight at room temperature and LiCl was filtered off. The solvent was then removed, the solid product residues extracted into about 15 mL of $CH_2Cl_2$, and crystals of each compound were grown over a two-day period at –80ºC.




**Scheme 5.3**. Synthesis of compounds **18-19.**

*Characterization*

Crystals of compounds **18** and **19** were each analyzed by a single crystal X-ray diffraction experiment. The results are shown in Figures 5.9 and 5.10.

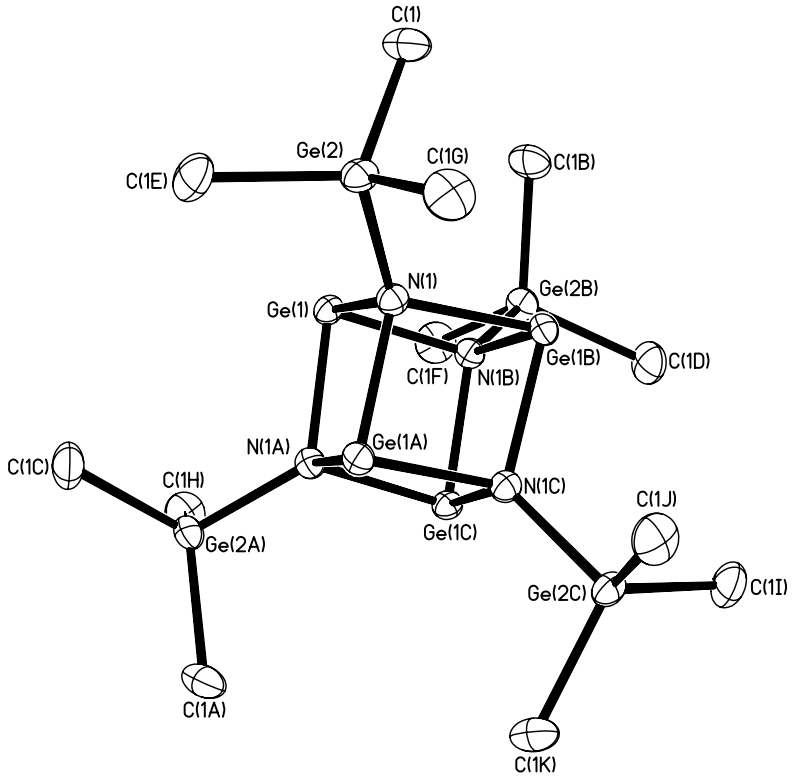



**Figure 5.9**. ORTEP plot representation (30% probability) with numbering scheme for compound **18**. Hydrogen atoms have been omitted for clarity.

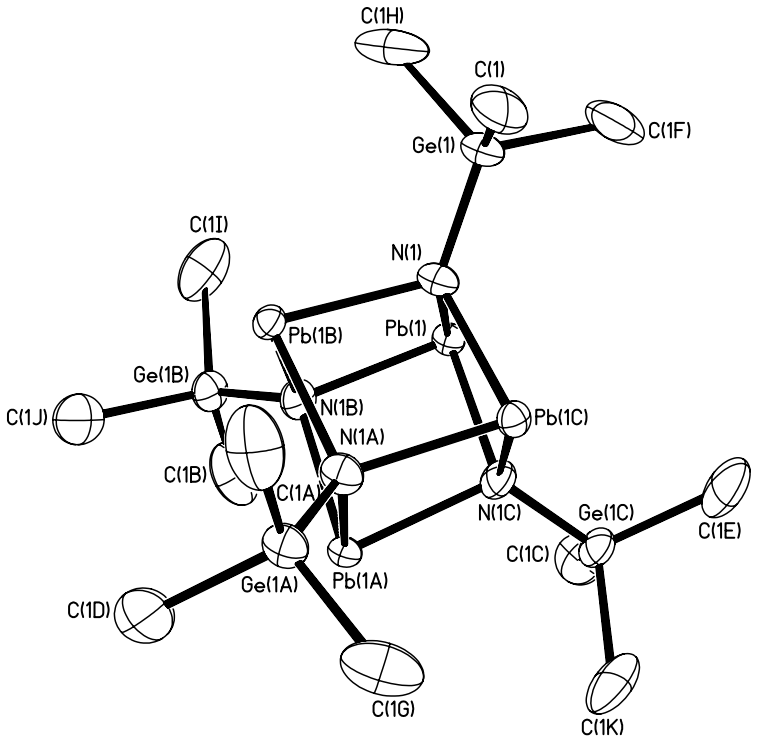



**Figure 5.10**. ORTEP plot representation (30% probability) with numbering scheme for compound **19**. Hydrogen atoms have been omitted for clarity.

Both complexes exist as tetramers in the solid state, with the trimethylgermyl imide units each bridging three divalent metal centers. A summary of the principal interatomic distances and angles for compounds **18** and **19** is provided in Table 5.4, and a complete list of all distances and angles can be found in Tables A.68 and A.72, respectively.

**Table 5.4**. Selected average interatomic distances (Å) and angles (degrees) for compounds **16**, **18**, and **19.**

| (**16**) | distance/angle | (**18**) | distance/angle | (**19**) | distance/angle |
|---|---|---|---|---|---|
| Ge-N | 1.860(12) | Ge-N | 1.870(9) | Ge-N | 1.850(2) |
| Sn-N (endo-cube) | 2.207(11) | Ge-N (endo-cube) | 2.002(4) | Pb-N (endo-cube) | 2.293(14) |
| Sn-N-Sn | 97.2(4) | Ge-N-Ge | 95.7(3) | Pb-N-Pb | 98.4(7) |
| N-Sn-N | 82.27(4) | N-Ge-N | 84.0(3) | N-Pb-N | 80.9(7) |

The molecular structure of compounds **18** and **19** were revealed by single-crystal X-ray diffraction techniques to be tetranuclear, based on a $M_4N_4$ architecture (Figure 5.6 and 5.7). Each nitrogen atom is four-coordinate, bridging three M(II) [M = Ge, Pb] metal centers and one germanium(IV) atom. The metal-nitrogen cage exhibits the typical distortion from perfect cube geometry, evidenced by the obtuse M-N-M angles and the acute N-M-N angles (see Table 5.4). The Ge(IV)-N interatomic distances of 1.870(9) Å and 1.850(2) Å (observed for **18** and **19**, respectively) are comparable to the previously reported value found in $(Li[N(GeMe_3)_2])_3$ [$Ge\text{-}N_{avg}$ = 1.837 Å].[11] The endo-cube M-N interatomic distances (M = Ge, Pb) also fall in the expected range observed in previous

Group 14-nitrogen heterocubanes: **18** [Ge-N = 2.002 Å]; $[GeN(C_6H_6)]_4$ [Ge-$N_{avg}$ = 2.023 Å];[5] **19** [Pb-N = 2.293 Å]; $[PbN(C_6H_{12})]_4$ [Pb-N = 2.303 Å][6] and $[PbN(2,6\text{-}i\text{-}Pr_2C_6H_3)]_4$ [Pb-N = 2.337 Å].[7]

Compounds **18** and **19**, along with compound **16** comprise an additional series of Group 14-nitrogen heterocubanes. Similar to the series of structures consisting of compounds **13**-**15**, the distortion in the $M_4N_4$ core observed in **16**, **18**, and **19** increases as the molecular weight of the Group 14 element increases (see Table 5.4). The occurrence of this phenomenon was previously discussed in Chapter 5 – Part A.

The volatility of compound **19** was determined by TGA. The cubane species is volatile below 300ºC, but appears to decompose at higher temperatures. The TGA plot of percent weight versus temperature is graphically depicted in Figure 5.11.

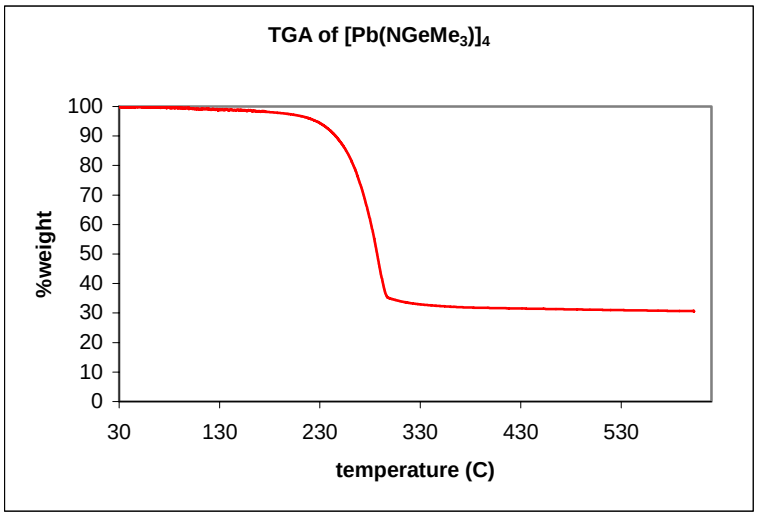



**Figure 5.11**. TGA plot of percent weight vs. temperature for compound **19**.

## Conclusion

The first three sections of this chapter have discussed the use of both the homoleptic lithiated bis(stannylamine) (**1**) and heteroleptic lithiated stannylamines [(**2**) and (**3**)] as precursors to Group 14-nitrogen heterocubanes. The successful molecular design of these compounds, accomplished by varying the endo-cube metal and exo-cube substituent has been demonstrated and the culmination of this design approach is described in this sub-chapter via the synthesis and characterization of **18** and **19**. The ultimate goal of extending this design motif to include titanium and zirconium cations for the preparation of ZTT precursors will be explored in the final section of this chapter.

## SECTION D: REACTION OF TIN-NITROGEN OXO OCUBANES WITH TETRAKIS TITANIUM ALKOXIDES: $Sn_6(\mu_3\text{-}O)_4(\mu_3\text{-}O^iPr)_4$ AND $Sn_6(\mu_3\text{-}O)_4(\mu_3\text{-}O^tBu)_4$

### Introduction

The first three sections of this chapter were devoted to exploring the use of lithiated stannylamines as precursors in the synthesis of Group 14-nitrogen heterocubanes and the subsequent molecular design of this class of compounds. Ideally, the incorporation of titanium or zirconium into either the endo-cube dication or exo-cube tetracation positions could potentially lead to MOCVD precursors for ZTT. However, dicationic titanium and zirconium are not synthetically useful species. In addition, trimethyl titanium chloride and trimethyl zirconium chloride reagents required to model the reactions described in the earlier sections of this chapter are not sufficiently stable at ambient conditions. Hence, an alternative design strategy is needed. The mixed-metal aminoalkoxide species previously reported by Veith, *et al*., $(^iPrO)_4Ti[OPb_4(N^tBu)_3]$[17] proved to be a model complex for a potential mixed-metal aminoalkoxide possessing tin and titanium. This sub-chapter describes the synthesis of the previously reported oxo cubane, $[Sn_4(N^tBu)_3O]$ (**20**)[18] and its reaction with tetrakis(alkoxide) titanium(IV) reagents. These reactions resulted in the isolation of the tin-oxygen cage structures $Sn_6(u_3\text{-}O)_4(u_3\text{-}O^iPr)_4$ (**21**) and $Sn_6(u_3\text{-}O)_4(u_3\text{-}O^tBu)_4$ (**22**). The synthesis and structural characterization of these compounds is described herein.

**Experimental**

All manipulations were carried out in a dry atmosphere glovebox or by standard Schlenk techniques. All solvents were dried over Na° metal and were freshly distilled under an inert atmosphere prior to use. $Ti(O^tBu)_4$ was purchased from Alfa Aesar and t-butylamine was purchased from Aldrich and both were used without further purification. $Sn(NMe_2)_2$ was prepared according to literature procedures.[19] Elemental analyses were performed in triplicate on a Perkin Elmer Series II CHNS/O Analyzer 2400 and FT-IR measurements were performed on a Bruker Equinox 55 Spectrometer.

*Synthesis of* $Sn_4O(N^tBu)_3 \bullet CH_3CN$ (**20**): Tertiary-butyl amine (0.43 g, 5.9 mmol) was added dropwise to a THF (25 mL) solution of $Sn(NMe_2)_2$ (1.21 g, 5.9 mmol) at room temperature and stirred for 2 hours. An acetonitrile (10 mL) solution of $H_2O$ (0.023 mL, 1.28 mmol) was then added dropwise, *in situ*, to the reaction mixture at –78ºC. The solution was allowed to attain ambient temperature on its own, stirred for an additional 2 hours, and subsequently filtered through a Schlenk frit. Finally, all volatile material was removed *in vacuo* and a bright yellow powder was isolated. Yield: 0.168 g (15%); IR (nujol): 2359 (w), 1377 (m), 1021 (m), 799 (m) $cm^{-1}$; elemental analysis calculated (%) for $C_{14}H_{30}N_4OSn_4$: C 22.57, H 4.06, N 7.52, found: C 22.46, H 4.37, N 7.33.

*Synthesis of* $Sn_6(\mu_3\text{-}O)_4(\mu_3\text{-}O^iPr)_4$ (**21**): Compound **20** (0.168 g, 0.24 mmol) was dispersed in hexane (20 mL) and to this was added a hexane solution of $Ti(O^iPr)_4$ (0.068 g, 0.24 mmol) at room temperature. The reaction mixture was stirred overnight under an

argon atmosphere and the solution was filtered through a Schlenk frit. Yellow crystals were grown overnight at –40ºC.

Crystal data for **21**. $C_{12}H_{28}O_8Sn_6$: $M_r$ = 1012.48 g cm$^{-3}$, crystal dimensions 0.14 x 0.12 x 0.10 mm, tetragonal, space group $I4(1)/a$, $a$ = 11.6029(10), $c$ = 18.017(3) Å, α = 90º; $V$ = 2435.6(5) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 2.773 g cm$^{-3}$, Siemens SMART CCD diffractometer, 2.09 ≤ $\theta$ ≤ 28.66˚, $Mo_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å), $\omega$ scans, $T$ = 193(2) K; of 6755 measured reflections, 1482 were independent and 987 observed with $I > 2\sigma(I)$, -15 ≤ $h$ ≤ 14, -11 ≤ $k$ ≤ 15, -24 ≤ $l$ ≤ 22; $R_1$ = 0.0283, $wR_2$ = 0.0582, GOF = 1.086 for 66 parameters, $\Delta\rho_{max}$ = 0.619 eÅ$^{-3}$. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-97), Lorentz polarization corrections and absorption correction (SADABS) were applied, $\mu$ = 6.114 mm$^{-1}$, min./max. transmission 0.5744/0.4902.

*Synthesis of $Sn_6(\mu_3\text{-}O)_4(\mu_3\text{-}O^tBu)_4$* (**22**): Compound **20** (0.168 g, 0.24 mmol) was dispersed in hexane (20 mL) and to this was added a hexane solution of $Ti(O^tBu)_4$ (0.082 g, 0.24 mmol) at room temperature. The reaction mixture was stirred overnight under an argon atmosphere and the solution was filtered through a Schlenk frit. Yellow crystals were grown overnight at –80ºC.

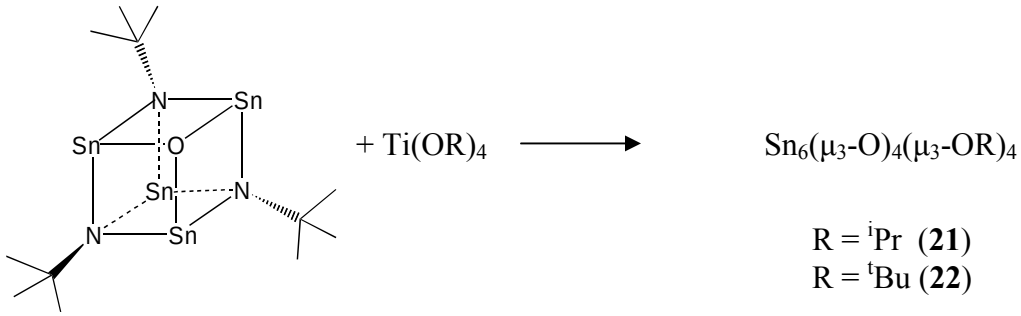
Crystal data for **22**. $C_{16}H_{36}O_8Sn_6$: $M_r$ = 1068.59 g cm$^{-3}$, crystal dimensions 0.31 x 0.15 x 0.14 mm, orthorhombic, space group *Pnma*, $a$ = 10.296(3), $b$ = 16.486(4), $c$ = 17.871(4) Å, α = 90º; $V$ = 3033.5(13) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 2.340 g cm$^{-3}$, Siemens SMART CCD diffractometer, 1.68 ≤ $\theta$ ≤ 28.96˚, $Mo_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å), $\omega$ scans, $T$ = 193(2) K; of 8628 measured reflections, 3517 were independent and 2974 observed with $I$ >

$2\sigma(I)$, $-5 \leq h \leq 13$, $-17 \leq k \leq 19$, $-23 \leq l \leq 23$; $R_1 = 0.0743$, $wR_2 = 0.1966$, GOF = 1.028 for 163 parameters, $\Delta\rho_{max} = 5.254$ eÅ$^{-3}$. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-97), Lorentz polarization corrections and absorption correction (SADABS) were applied, $\mu = 4.895$ mm$^{-1}$, min./max. transmission 0.5557/0.3158.

**Results and Discussion**

*Synthesis*

Compound **20** was synthesized as previously reported by Wright and coworkers.[18] The synthesis of compounds **21** and **22** is shown in Scheme 5.4. Both compounds were prepared by carefully adding a hexane solution of the appropriate tetrakis titanium alkoxide to an equimolar amount of compound **20** at room temperature. The reaction mixture was stirred overnight and filtered to afford a clear, yellow solution. Yellow crystals of compounds **21** and **22** were grown from the hexane reaction solution overnight at –40ºC and –80ºC, respectively.




**Scheme 5.4**. Synthesis of compounds **21-22.**

*Characterization*

Crystals of compounds **21** and **22** were each analyzed by a single crystal X-ray diffraction experiment. The results are shown in Figures 5.12 and 5.13.

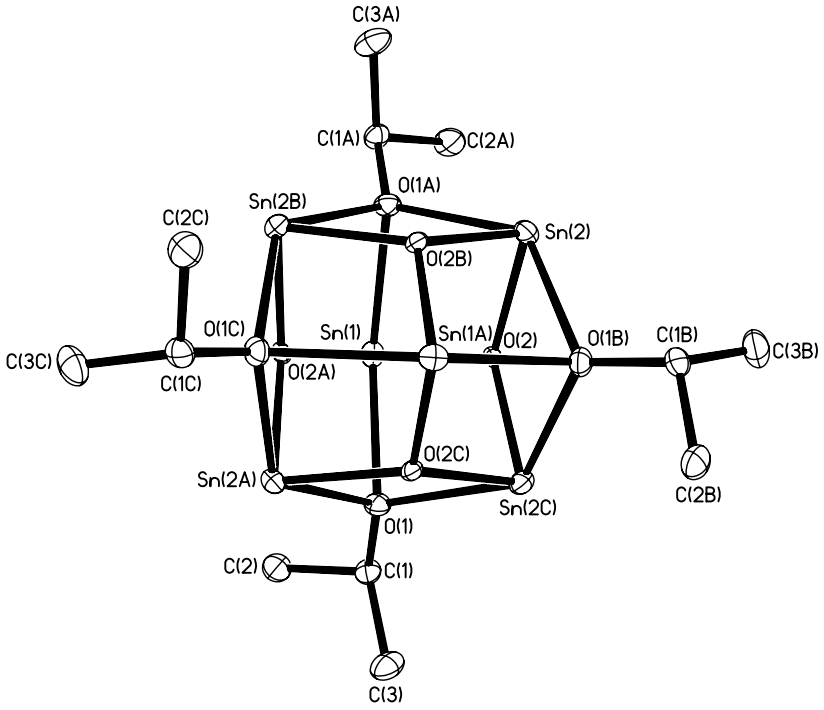



**Figure 5.12**. ORTEP plot representation (30% probability) with numbering scheme for compound **21**. Hydrogen atoms have been omitted for clarity.

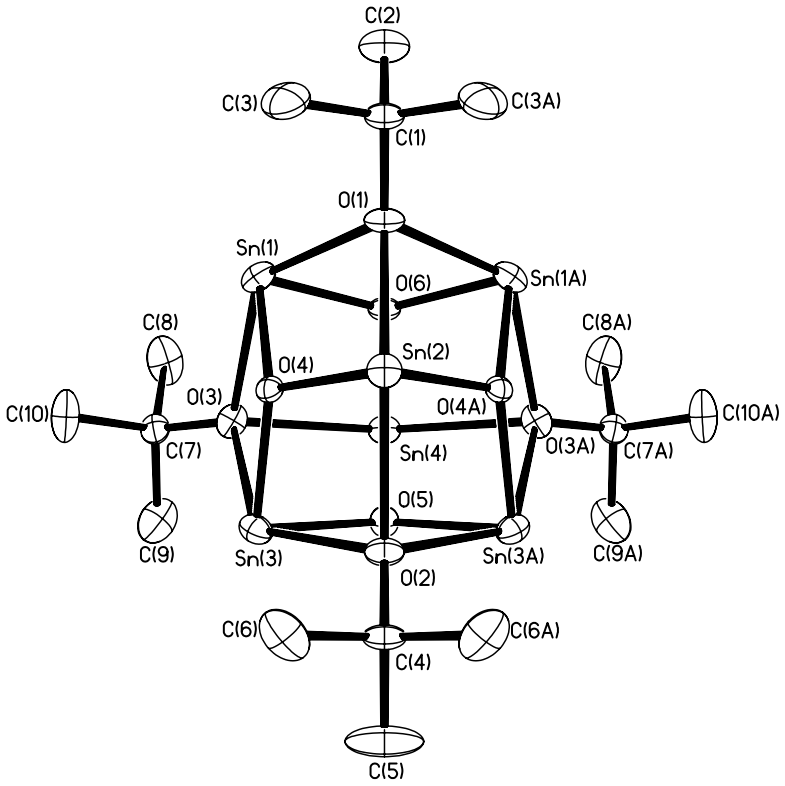



**Figure 5.13**. ORTEP plot representation (30% probability) with numbering scheme for compound **22**. Hydrogen atoms have been omitted for clarity.

Instead of obtaining the expected bimetallic aminoalkoxides, $(^{i}PrO)_4Ti[OSn_4(N^{t}Bu)_3]$ or $(^{t}BuO)_4Ti[OSn_4(N^{t}Bu)_3]$, the hexameric tin species **21** and **22** were isolated. It is noted that due to the limited yields of compound **20**, extensive characterization of this intermediate beyond elemental analysis was not carried out. Given this fact, the identity of **20** as depicted in Scheme 5.4 cannot be reported here with complete confidence. Thus, an explanation for the unanticipated formation of **21** and **22** cannot be formulated without obtaining additional data.

As seen in Figures 5.12 and 5.13, these compounds are comprised of tin hexamers, with each tin(II) metal center being coordinated by two $(\mu_3\text{-}O)^{-2}$ and two $(\mu_3\text{-}O^{t}Bu)^{-1}$ ligands. The structures can best be described as being comprised of two $[Sn_2(\mu_2\text{-}O)(\mu_2\text{-}OR)]$ dimers that are bridged by two $Sn^{+2}$ cations, two $O^{-2}$ atoms, and two $RO^{-1}$ ligands. These types of structures are not unprecedented, as compound **21**[20] and the analogous compounds $Sn_6(\mu_3\text{-}O)_4(\mu_3\text{-}OC_5H_{11})_4$[21] and $Sn_6(\mu_3\text{-}O)_4(\mu_3\text{-}OCH_3)_4$[22] have been previously synthesized and structurally characterized. However, these three species were synthesized via a different pathway than that reported here in this sub-chapter. The pertinent interatomic distances for **21** and **22** are listed in Table 5.5 and all of the interatomic distances and angles can be found in Tables A.76 and A.80, respectively. The Sn-O and Sn-OR distances are within the range observed in the structural analogues previously reported (see Table 5.6).

**Table 5.5**. Selected average interatomic distances (Å) and angles (degrees) for compounds **21** and **22.**

| (**21**) | distance | (**22**) | distance |
|---|---|---|---|
| Sn-O | 2.082(3) | Sn-O | 2.074(8) |
| Sn-O$^{i}$Pr | 2.393(3) | Sn-O$^{t}$Bu | 2.393(8) |

**Table 5.6**. Selected average interatomic distances (Å) and angles (degrees) for compounds $Sn_6(u_3\text{-}O)_4(u_3\text{-}OCH_3)_4$ and $Sn_6(u_3\text{-}O)_4(u_3\text{-}OC_5H_{11})_4$**.**

| $Sn_6(u_3\text{-}O)_4(u_3\text{-}OCH_3)_4$ | distance | $Sn_6(u_3\text{-}O)_4(u_3\text{-}OC_5H_{11})_4$ | distance |
|---|---|---|---|
| Sn-O | 2.067 | Sn-O | 2.083 |
| Sn-OR | 2.379 | Sn-OR | 2.447 |

**Conclusion**

In an attempt to prepare bi-metallic aminoalkoxides, the oxocubane species **20** was reacted with tetrakis(alkoxide) titanium(IV). Aminoalkoxides of this type would potentially serve as useful precursors in the MOCVD of ZTT. However, instead of obtaining tin-titanium heterometallic aminoalkoxides, the hexameric tin species **21** and **22** were produced. Such species will not likely show utility in MOCVD applications. Thus, alternative synthetic routes to tin-titanium heterometallic compounds will be pursued in future chapters.

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# CHAPTER 6

# THE MOCVD OF ZTT VIA THE USE OF TIN-TITANIUM ALKOXIDE-AMIDES

## SECTION A: SYNTHESIS AND CHARACTERIZATION OF HETEROMETALLIC ALKOXIDE-AMIDES FOR USE AS PRECUSRORS IN THE CVD OF ZTT: $(Me_3Sn)(Me_3E)Ti(OR)_3$ [E = Sn, Si; R = $^{i}$Pr, $^{t}$Bu, NeoPe]

### Introduction

As was discussed in Chapter 1, decreasing dimensions in integrated circuit (IC) design have driven the need for high dielectric constant (high-*k*) materials to replace $SiO_2$ ($k \sim 4$) as the gate oxide. For various reasons, particularly integration issues, the replacement of $SiO_2$ as the gate oxide material proves to be extraordinarily difficult. Although several binary metal oxide, oxynitride, and silicate compounds have been studied as alternative gate oxide materials, only few can meet all of the rigorous demands placed upon high-*k* dielectrics in silicon-based devices. Specifically, it is of great importance to find gate oxide materials that display sufficiently low leakage currents, which aids in decreasing the overall power consumption of the device.[1,2]

A recent entry into the group of potential alternative dielectric materials is zirconium-tin-titanate (ZTT). High-*k* ZTT films were initially prepared via Magnetron sputtering by van Dover, *et al*., and the results of their work suggested that this material may be a viable candidate for use in CMOS devices.[3] More recently, MOCVD has been used by Senzaki, *et al*., as well as researchers in our laboratory, to fabricate thin films of

ZTT.[4,5] In a recent report, ZTT thin films were made by using a solvent-free precursor mixture comprised of $Zr(OBu^t)_4$, $Sn(OBu^t)_4$, and $Ti(OBu^t)_4$.[4] The precursor was transported to a cold-walled reactor via a direct liquid injection system and then introduced onto the heated silicon substrate by a vaporizer. ZTT thin films were grown between 350ºC and 390ºC and as-deposited materials were found to have dielectric constants ranging from 20-27.[5]

It is believed that properties of metal oxide films, such as dielectric constant, are governed by the ratio of metal cations present in the final material, and control over the cation ratio in the final film can be achieved by manipulating the nature of the precursors. Thus, it is of interest to design an alternative precursor system for the MOCVD of ZTT, with the ultimate aim being the increase of the dielectric constant and reduction of the leakage current. One approach is to synthesize heterometallic precursors possessing two or more of the metals of interest. If the ratio of metal cations is fixed in the precursor molecule, then better control of the cations in the final material can be achieved.[6]

As described earlier in this work, the lithiated stannylamine, $[(Me_3Sn)_2NLi•THF]$ can be used in the synthesis of heterometallic coordination compounds. Hence, the reactions of both homoleptic $[(Me_3Sn)_2NLi•THF]$ and heteroleptic $[(Me_3Sn)(Me_3Si)NLi•Et_2O]$ lithiated stannylamines with tris(alkoxide)titanium(IV) chloride species were carried out and resulted in the production of the heterometallic alkoxide-amides $(Me_3Sn)_2NTi(O^iPr)_3$ (**23**), $(Me_3Sn)_2NTi(O^tBu)_3$ (**24**), $(Me_3Sn)(Me_3Si)NTi(O^iPr)_3$ (**25**), and $(Me_3Sn)_2NTi(OC_5H_{11})_3$ (**27**). Details of the synthesis and characterization of this series of compounds are described herein.

**Experimental**

All manipulations were carried out in a dry atmosphere glovebox or by standard Schlenk techniques. All solvents were dried over Naº metal and were freshly distilled under an inert atmosphere prior to use. $(^{i}PrO)_3TiCl$ was purchased from Alfa Aesar and used without further purification. $[(Me_3Sn)_2NLi\bullet(THF)]_2$ and $[(Me_3Sn)(Me_3Si)NLi\bullet(Et_2O)]_2$ were prepared as described in Chapter 2. $(^{t}BuO)_3TiCl$ was prepared according to literature procedures.[7] All NMR experiments were performed on a Bruker 400 MHz Spectrometer at 300K using $C_6D_6$ solvent that was distilled over $CaH_2$ and stored under argon. $^{1}H$, $^{13}C$, and $^{29}Si$ spectra were referenced to TMS. $^{119}Sn$ spectra were externally referenced to $Me_4Sn$. All elemental analyses were performed in triplicate on a Perkin Elmer Series II CHNS/O Analyzer 2400. All FT-IR measurements were performed on a Bruker Equinox 55 Spectrometer. All mass spectrometry analyses were done on a VG Instruments 70SE (Electron Impact; 70eV). All TGA experiments were performed on a Perkin Elmer 7/DX thermal analyser interfaced to a Perkin Elmer Thermal Analysis Controller (TAC). The instrument is housed in a dry atmosphere glovebox. Argon was used as the purge gas and all %weight vs. temperature profiles were done at a 10ºC/min. temperature ramp under ambient pressure.

*Synthesis of $(Me_3Sn)_2NTi(O^{i}Pr)_3$* (**23**): A diethyl ether (30 mL) solution of $[(Me_3Sn)_2NLi\bullet(THF)]_2$ (2.00 g, 2.38 mmol) was added dropwise to a diethyl ether slurry of $(^{i}PrO)_3TiCl$ (1.24 g, 4.76 mmol) at 0ºC. The reaction mixture was allowed to attain ambient temperature on its own and a colorless precipitate formed within 15 minutes.

The reaction was stirred overnight under an argon atmosphere and was filtered through a Schlenk frit, resulting in a clear yellow solution. The solvent was removed from the filtrate *in vacuo* and the residual oil was distilled under vacuum (70-75ºC, 0.01 Torr) to give a colorless liquid. Yield: 1.52 g (57%); $^{1}$H NMR (400 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ 0.27 (d, 18 H, $SnCH_3$), 1.23 (d, 18 H, $CH_3$), 1.01 (m, 3 H, CH); $^{13}$C NMR (100.6 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ –3.55 (d, $SnCH_3$), 26.90 (d, $CH_3$), 75.00 (d, CH), $^{119}$Sn NMR (149.3 MHz, $C_6D_6$, 25ºC, $Me_4Sn$): $\delta$ 78.0 (d, $SnCH_3$); MS (EI, 110°C): *m/z* 551 [(M-15)$^{+}$]; elemental analysis calculated (%) for $C_{15}H_{39}NO_3Sn_2Ti$: C 31.79, H 6.94, N 2.47, found: C 31.30, H 7.05, N 2.80.

*Synthesis of $(Me_3Sn)_2NTi(O^tBu)_3$* (**24**): Compound **24** was prepared in an analogous fashion to compound **23** using $[(Me_3Sn)_2NLi\bullet(THF)]_2$ (2.00 g, 2.38 mmol) and $(^tBuO)_3TiCl$ (1.44 g, 4.76 mmol). The product was distilled (75-80ºC, 0.01 Torr) to produce a colorless liquid. Yield: 1.69 g (58%); $^{1}$H NMR (400 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ 0.21 (s, 18 H, $SnCH_3$), 1.35 (s, 27 H, $CH_3$); $^{13}$C NMR (100.6 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ –1.49 (s, $SnCH_3$), 32.46 (s, $CH_3$), 79.99 (s, $C(CH_3)_3$), $^{119}$Sn NMR (149.3 MHz, $C_6D_6$, 25ºC, $Me_4Sn$): $\delta$ 89.8 (s, $SnCH_3$); elemental analysis calculated (%) for $C_{18}H_{45}NO_3Sn_2Ti$: C 35.51, H 7.45, N 2.30, found: C 35.32, H 7.44, N 2.46.

*Synthesis of $(Me_3Sn)(Me_3Si)NTi(O^iPr)_3$* (**25**): Compound **25** as prepared in an analogous fashion to compound **23** using $[(Me_3Sn)(Me_3Si)NLi\bullet(Et_2O)]_2$ (2.00 g, 3.07 mmol) and $(^iPrO)_3TiCl$ (1.60 g, 6.14 mmol). The product was isolated as a yellow oil after removal of solvent under vacuum. Yield: 1.55 g (54%); $^{1}$H NMR (400 MHz, $C_6D_6$, 25ºC, TMS):

$\delta$ 0.15 (d, 9 H, $SiCH_3$), 0.34 (d, 9 H, $SnCH_3$), 1.12 (m, 18 H, $CH_3$), 4.47 (m, 3 H, CH); $^{13}C$ NMR (100.6 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ –1.78 (s, $SiCH_3$), 4.78 (s, $SnCH_3$), 26.7 (s, $CH_3$), 76.3 (s, CH); $^{119}Sn$ NMR (149.3 MHz, $C_6D_6$, 25ºC, $Me_4Sn$): $\delta$ 66.7 (s, $SnCH_3$), $^{29}Si$ NMR (79 MHz, $C_6D_6$, 25ºC, $Me_4Si$): $\delta$ 5.53 (s, $SiMe_3$); elemental analysis calculated (%) for $C_{15}H_{39}NO_3SnSiTi$: C 37.84, H 8.26, N 2.94, found: C 38.24, H 8.82, N 3.42.

*Synthesis of $(C_5H_{11}O)_3TiCl$* (**26**): A toluene solution of $TiCl_4$ (1.91 g, 4.8 mmol) was added dropwise at room temperature to a toluene (30 mL) solution of $(C_5H_{11}O)_4Ti$ ( 0.30 g, 1.6 mmol). The reaction mixture was then brought to reflux and stirred overnight in an argon atmosphere. All volatile materials were subsequently removed *in vacuo* and a colorless solid was isolated. Attempts to grow crystals of this material were not successful. Yield: 1.21 g (55%); elemental analysis calculated (%) for $C_{15}H_{33}O_3ClTi$: C 52.26, H 9.65, found: C 51.34, H 9.67.

*Synthesis of $(Me_3Sn)_2NTi(OC_5H_{11})_3$* (**27**): A diethyl ether (30 mL) solution of $[(Me_3Sn)_2NLi\bullet(THF)]_2$ (0.87 g, 2.00 mmol) was added dropwise to a diethyl ether slurry of **26** (0.64 g, 2.00 mmol) at 0ºC. The reaction mixture was allowed to attain ambient temperature on its own and a colorless precipitate formed within 15 minutes. The reaction was stirred overnight under an argon atmosphere and was filtered through a Schlenk frit, resulting in a clear yellow solution. Finally, the solvent was removed from the filtrate *in vacuo,* resulting in the isolation of a yellow oil. Yield: 0.75 g (59%); $^1H$ NMR (400 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ 0.41 (s, 18 H, $SnCH_3$), 1.01 (s, 27 H, $CH_3$), 4.08

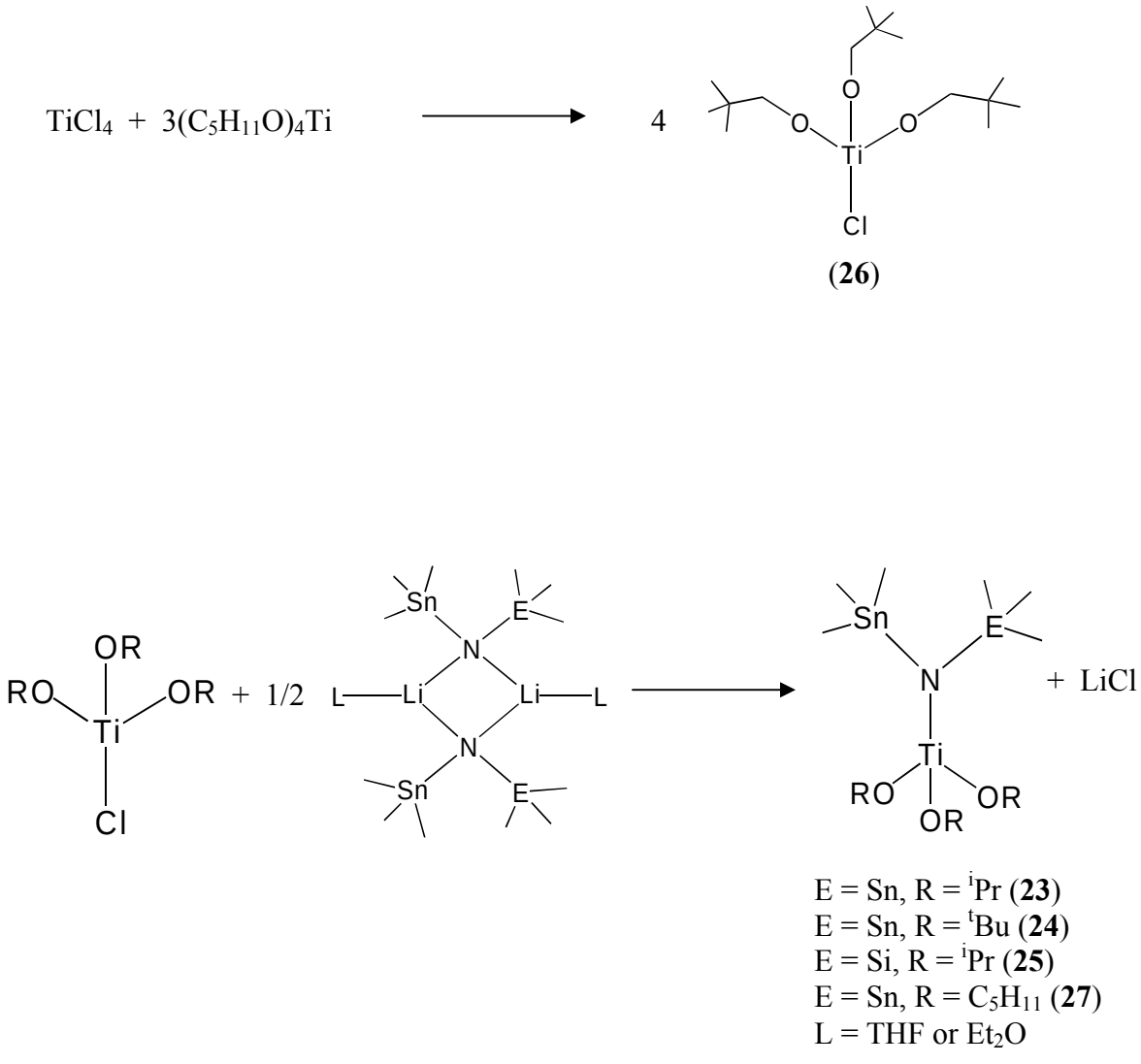
(s, 6 H); $^{13}$C NMR (100.6 MHz, $C_6D_6$, 25ºC, TMS): $\delta$ –1.78 (s, $SnCH_3$), 26.61 (s, $CH_3$), 34.26 (s, -C-), 85.67 (s, -$CH_2$-); $^{119}$Sn NMR (149.3 MHz, $C_6D_6$, 25ºC, $Me_4Sn$): $\delta$ 70.3 (s, $SnCH_3$); elemental analysis calculated (%) for $C_{21}H_{51}NO_3Sn_2Ti$: C 38.75, H 7.90, N 2.15, found: C 38.07, H 8.07, N 2.62.

**Results and Discussion**

*Synthesis*

Tris(alkoxide)titanium(IV) chlorides can be prepared by the comproportionation reaction between titanium tetrachloride and titanium tetrakis alkoxides. For the purposes of this work, the isopropyl derivitive was purchased, the tertiarybutyl congener synthesized according to previous literature reports,[7] and the neopentoxide species (**26**) prepared by the method depicted in Scheme 6.1. Compound **26** was obtained by the reaction of one equivalent of titanium tetrachloride with three equivalents of tetrakis(neopentoxide)titanium(IV) in a refluxing solution of toluene. After stirring overnight under reflux, the volatile materials were removed *in vacuo* and a colorless solid material was isolated.

Compounds **23**-**25** and **27** were analogously prepared by reacting each tris(alkoxide)titanium(IV) chloride with 0.5 equivalents of the appropriate lithiated stannylamine (see Scheme 6.1). The reaction mixture was stirred overnight at room temperature and the resulting LiCl precipitate was filtered off. The solvent was then distilled off at ambient pressure, and the final liquid product was either distilled under vacuum (compounds **23**-**24**) or dried under reduced pressure (compounds **25** and **27**).




**Scheme 6.1**. Synthesis of compounds **23-27.**

*Characterization*

The structures of compounds **23-27,** depicted in Scheme 6.1, are consistent with the multinuclear NMR and elemental analysis data. Since **23** and **24** are distillable liquids exhibiting significant volatility, it can be surmised that these species exist as monomers in the liquid state. Empirical evidence to support this notion is found in the mass spectrum of compound **23**. A molecular ion peak [$(M-15)^+$] is observed in the electron impact (EI) mass spectrum at m/z = 551, the mass of the monomeric congener after the loss of one methyl fragment. The mass spectra obtained for compounds **24** and **25** gave inconclusive results. In solution, compounds **23** and **25** potentially undergo a dynamic conversion from monomer to dimer, evidenced by the splitting of the $Sn(CH_3)_3$ methyl peaks in the $^1H$ NMR. However, variable temperature $^1H$ NMR of compound **23** shows no coalescence of these peaks at higher temperatures (Figure 6.1). One possible explanation for the splitting of these peaks may be due to a difference in symmetry between compounds **23** and **25** and compound **24**.

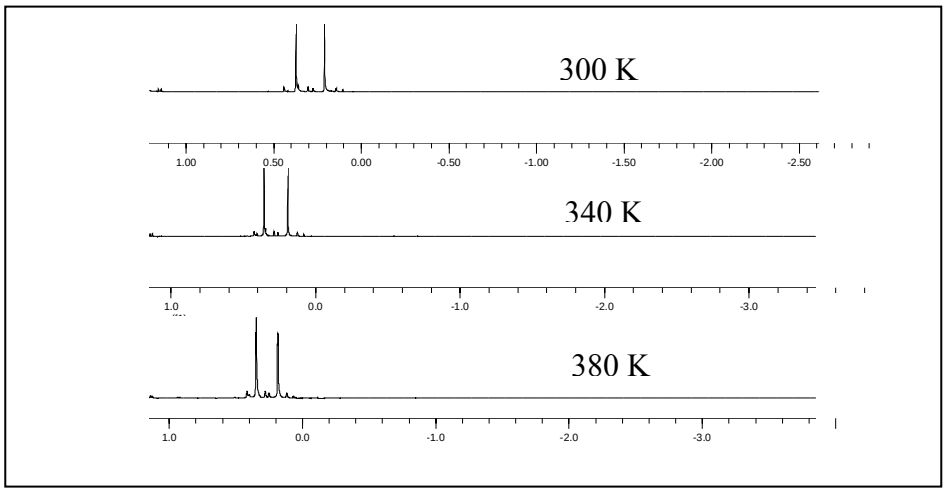



**Figure 6.1**. Variable temperature $^1H$ NMR of compound **23**: -$Sn(CH_3)_2$ peaks shown (chemical shift scale in ppm).

The thermal properties of compounds **23**-**25** were examined by thermogravimetric analysis (TGA). The results of these analyses are summarized in Figure 6.2. All three compounds show significant volatility below 200ºC at atmospheric pressure. Compounds **23** and **24** exhibit single-step mass losses with residual percent weight values below 10%. Compound **25** also shows a single-step mass loss, but appears to undergo decomposition when approximately 20% of the sample mass remains. A qualitative comparison of the TGA plots indicates a trend of increasing volatility for the alkoxide-amides in the order: **24** > **23** > **25**. An explanation for this trend can be found in the steric bulk present on all three complexes. Compound **24**, having two trimethyl stannyl moieties bound to nitrogen and three tert-butoxides bound to titanium, has the most steric protection around the titanium metal center, thereby limiting intermolecular interactions and increasing its volatility. Compound **23**, with two trimethyl stannyl moieties bound to nitrogen and three iso-propoxides bound to titanium, effectively has less steric protection than **24**. Finally, compound **25**, with one trimethyl stannyl and one trimethyl silyl group bound to nitrogen, along with three iso-propoxides bound to titanium effectively has less steric protection than **23**.

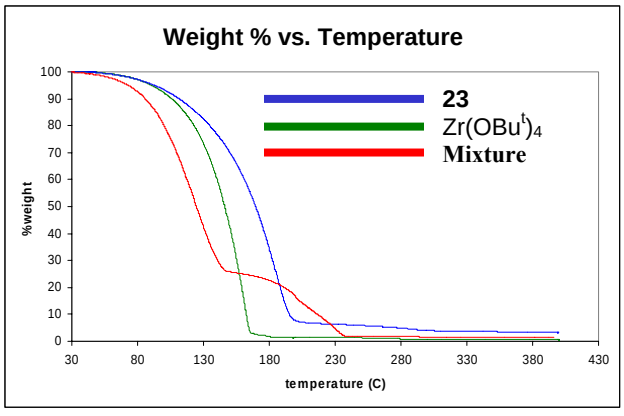
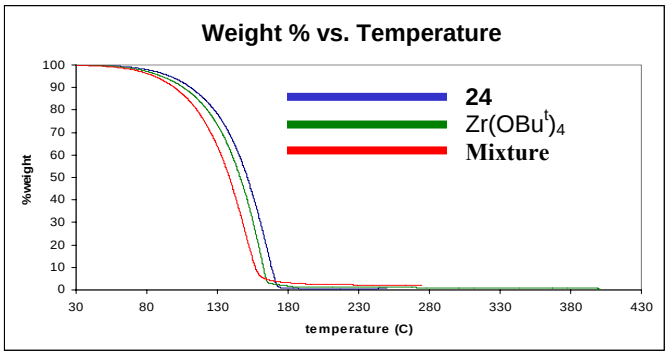
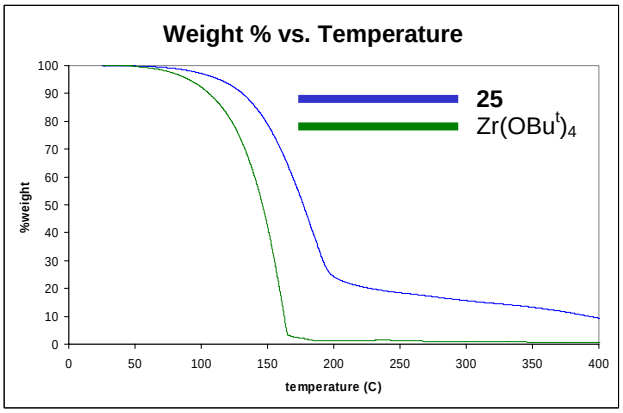



**Figure 6.2**.**A**. TGA plots of compound **23**, Zr(OBu$^t$)$_4$, and a mixture of the two species.




A




B

**Figure 6.2.B**. TGA plot of A: compound **24**, $Zr(OBu^t)_4$, and a mixture of the two species B: compound **25** and $Zr(OBu^t)_4$.

Since it was desired to deposit ZTT films using compounds **1-3** in combination with $Zr(OBu^t)_4$, the TGA profile of zirconium tert-butoxide is also provided in Figure 6.2. Separate TGA experiments for compounds **23-25** are plotted adjacent to the $Zr(OBu^t)_4$ TG curve. It is evident that compound **24** closely matches zirconium tert-butoxide in volatility. In addition, equimolar mixtures of $Zr(OBu^t)_4$ with compounds **23** and **24** were analyzed. It can be seen in Figure 6.2 that the mixture with **24** gives a single-step mass loss, whereas the mixture with **23** gives a two-step mass loss. Whether the two-step mass loss observed in the latter case is caused by interaction of the aminoalkoxide with $Zr(OBu^t)_4$, or because **23** has slightly lower volatility remains to be determined. Based on the thermal analyses, compounds **23-25** appear to be viable candidates for utilization in conjunction with $Zr(OBu^t)_4$ in the MOCVD of ZTT.

**Conclusion**

The synthesis and characterization of a series of heterometallic alkoxide-amides (compounds **23-26** and **27**) possessing both tin and titanium has been carried out in an attempt to prepare MOCVD precursors of ZTT containing more than one of the desired cations. During the course of this study, it was found that compounds **23-25** possess similar volatilities to $Zr(OBu^t)_4$, making the combination of these compounds a viable precusor cocktail for the MOCVD of ZTT.

## SECTION B: CVD OF ZTT USING BIS(TRIMETHYLSTANNYL)AMIDE TITANIUM(IV) TRIS(ALKOXIDES)

### Introduction

In Chapter 6 – Part A the series of heterometallic alkoxide-amides, $(Me_3Sn)_2NTi(O^iPr)_3$ (**23**), $(Me_3Sn)_2NTi(O^tBu)_3$ (**24**), and $(Me_3Sn)(Me_3Si)NTi(O^iPr)_3$ (**25**) were found to be viable precursors for the MOCVD of ZTT. This conclusion was based on the thermogravimetric analysis of **23**-**25** and $Zr(O^tBu)_4$, which have subsequently been employed in tandem in the MOCVD of ZTT. The deposition of ZTT thin films and their characterization via X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM) is described herein.

### Experimental

All depositions were performed with a low-pressure, hot-walled tube furnace reactor, which is schematically depicted in Figure 6.2. Ultra high purity nitrogen and oxygen gases were purchased from AirGas and used without further scrubbing. The system is comprised of a quartz tube (2 cm internal diameter), housed in a Lindberg Blue M Furnace, which is interfaced with a MKS Instruments Type 631 Baratron Pressure Transducer (with MKS Instruments Type 250 Controller and Readout) and Welch 5 vacuum pump. The precursor delivery line is interfaced with two MKS Instruments Mass-Flo® gas flow controllers, one that controls the flow of nitrogen carrier gas into the precursor reservoir, and another that controls the flow of oxygen into the reactor chamber. For all depositions, a silicon wafer (approximately 1.5 cm x 1.5 cm) was

placed in a 10% aqueous HF solution for 5 minutes. The wafer was dried by evaporation, placed on a porcelain base, and then inserted into the quartz tube furnace. At this point, the furnace was placed under vacuum and the detachable precursor reservoir was taken into a dry atmosphere glovebox. The precursors were weighed into glass vials and loaded into the reservoir, the reservoir valves closed, and the entire apparatus transported and attached to the reactor. Once the furnace, precursor delivery lines, and precursor reservoir were brought to the appropriate temperature, the carrier gas and oxygen gas were turned on and the valves to the precursor reservoir opened. The experimental conditions for each deposition are summarized in Table 6.1.

*ZTT thin films*: Films **1**-**5** were analyzed as deposited. All SEM pictures were obtained on a Leo 1530 thermally assisted FEG scanning electron microscope. All X-ray Photoelectron Spectroscopy (XPS) measurements were performed on a PHI 1600/3057 with a standard aluminum x-ray source. The atomic concentration of the films deposition in runs 1-5 are summarized in Table 6.2.

**Results and Discussion**

A schematic of the MOCVD system is depicted in Figure 6.3 and the experimental conditions for each deposition are summarized in Table 6.1. To avoid decomposition, the precursors were loaded into a vial and sealed in the detachable reservoir inside a dry atmosphere glovebox. Then, the reservoir was attached to the reactor while still under argon. Once the desired temperature of the reservoir was attained, the nitrogen carrier gas and oxygen gas were turned on and the reservoir opened up to the system. Once the deposition was complete, the wafer was allowed to slowly reach ambient temperature

while under a nitrogen atmosphere and then stored in a vacuum desiccator until further characterization was carried out. Experiments 1 and 3 used a physical mixture of the amidoalkoxide and zirconium tert-butoxide liquids, and experiments 2, 4, and 5 were performed using separate vials for each precursor.

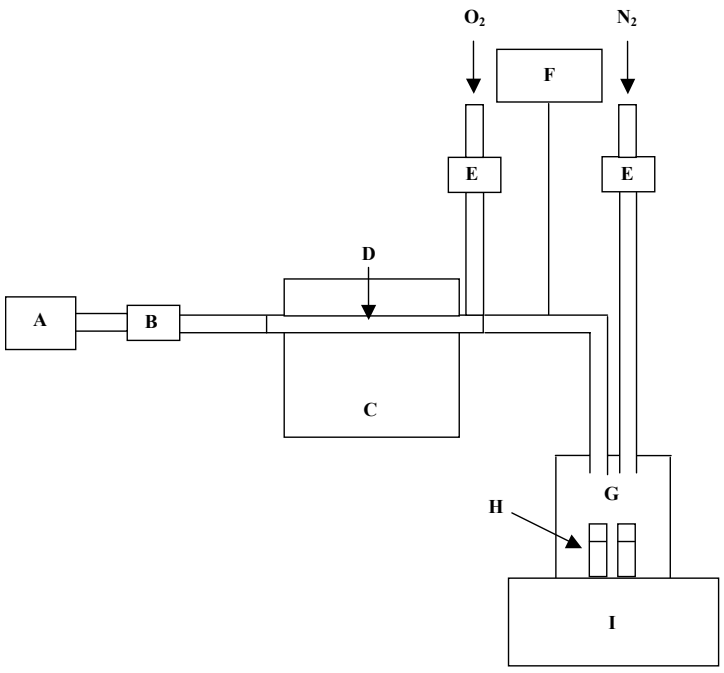



**Figure 6.3**. Schematic of MOCVD reactor (**A**: vacuum pump **B**: pressure transducer **C**: furnace **D**: quartz tube **E**: gas flow controllers **F**: precursor delivery line temperature controller **G**: detachable precursor reservoir **H**: vials containing liquid precursor **I**: heating plate).

**Table 6.1**. Experimental conditions for the MOCVD of ZTT using precursors **23**-**25** and $Zr(OBu^t)_4$.

| deposition | precursor system | precursor resevoir temp. | delivery line temp. | furnace temp. | pressure | carrier gas flow | oxygen gas flow | deposition time |
|---|---|---|---|---|---|---|---|---|
| experiment 1 | **23** (0.2g)/ $Zr(OPr^i)_4$(0.2g) mixed | 70ºC | 100-120ºC | 430ºC | 6.4 Torr | 200 sccm | 100 sccm | 30 min. |
| experiment 2 | **23** (0.2g)/ $Zr(OPr^i)_4$(0.2g) separate | 75ºC | 100-120ºC | 430ºC | 5.5 Torr | 200 sccm | 100 sccm | 30 min. |
| experiment 3 | **24** (0.1g)/ $Zr(OPr^i)_4$(0.1g) mixed | 55ºC | 100-120ºC | 430ºC | 6.5 Torr | 200 sccm | 100 sccm | 30 min. |
| experiment 4 | **24** (0.2g)/ $Zr(OPr^i)_4$(0.2g) separate | 60ºC | 100-120ºC | 430ºC | 6.2 Torr | 200 sccm | 100 sccm | 30 min. |
| experiment 5 | **25** (0.1g)/ $Zr(OPr^i)_4$(0.1g) separate | 65ºC | 100-120ºC | 430ºC | 6.4 Torr | 200 sccm | 100 sccm | 30 min. |

X-ray photoelectron spectroscopy (XPS) was performed on the films obtained from MOCVD experiments 1-5. High resolution spectra were recorded and the atomic concentration, as well as the molar composition of each film is summarized in Table 6.2. All compositional data is relevant only for the film surface due to the fact that ion sputtering was not available at the time of analysis. The films obtained from experiments 1-3, and 5 lacked the presence of zirconium in the film. However, films from experiments 1, 3, and 5 showed the presence of both tin and titanium, indicating that the aminoalkoxide precursor delivered the cations to the substrate. Experiment 4 gave the

most encouraging results in that all three metals were found to be in the oxide material, suggesting that the compound **24** is best suited to be used along with $Zr(OBu^t)_4$ in the MOCVD of ZTT. Whether the lack of zirconium in films 1-3 and 5 is due to precursor incompatibility or limitations in the MOCVD reactor system has not been determined at this time. All films exhibited carbon contamination (ranging from 17-24%), however it is possible that this arises from ambient carbon sources. XPS spectra need to be obtained after plasma sputtering to determine the sub-surface atomic content.

**Table 6.2**. Atomic concentration and molar composition of ZTT films calculated from high resolution XPS measurements.

| film | %Zr3d | %Sn3d5 | %Ti2p | %O1s | %C1s | molar composition |
|---|---|---|---|---|---|---|
| experiment 1 | 0.00 | 2.10 | 17.55 | 44.80 | 20.22 | $Sn_{0.02}Ti_{0.37}O_{2.80}$ |
| experiment 2 | 0.00 | 23.88 | 0.00 | 52.87 | 23.25 | $Sn_{0.20}O_{3.31}$ |
| experiment 3 | 0.00 | 12.23 | 9.27 | 53.80 | 24.69 | $Sn_{0.10}Ti_{0.19}O_{3.36}$ |
| experiment 4 | 8.85 | 13.73 | 2.18 | 53.81 | 21.41 | $Zr_{0.97}Sn_{0.12}Ti_{0.05}O_{3.33}$ |
| experiment 5 | 0.00 | 8.67 | 13.94 | 59.72 | 17.67 | $Sn_{0.07}Ti_{0.29}O_{3.73}$ |

The ZTT thin films were also characterized by SEM (micrographs of films 1 and 4 are shown in Figure 6.4). All films possessed smooth surfaces comprised of regularly arrayed, homogeneous crystallites. The size of the crystallites varied between films, and ranged in size from about 20 nm to 200 nm. Some of the films contained larger, heterogeneous particles that could have been ablated contaminants from the reactor wall.

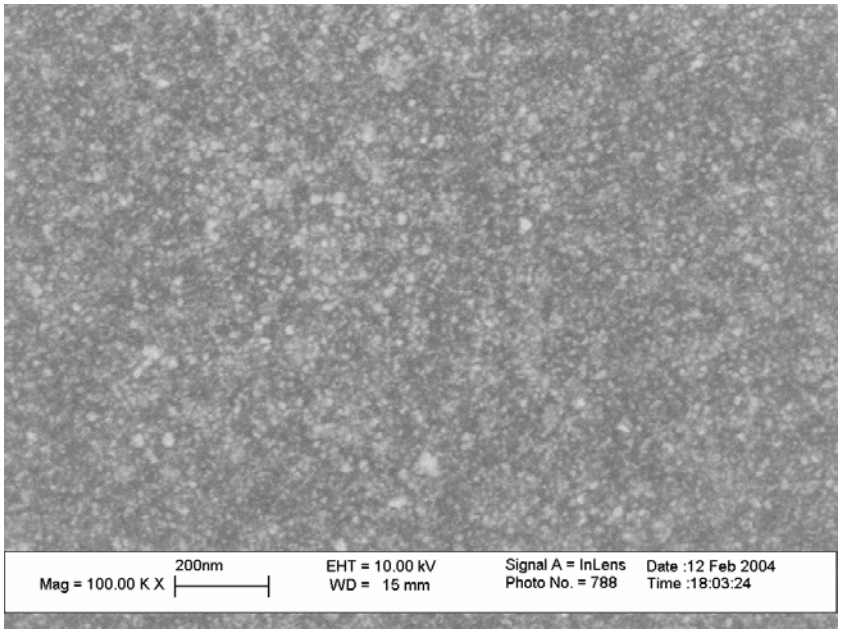
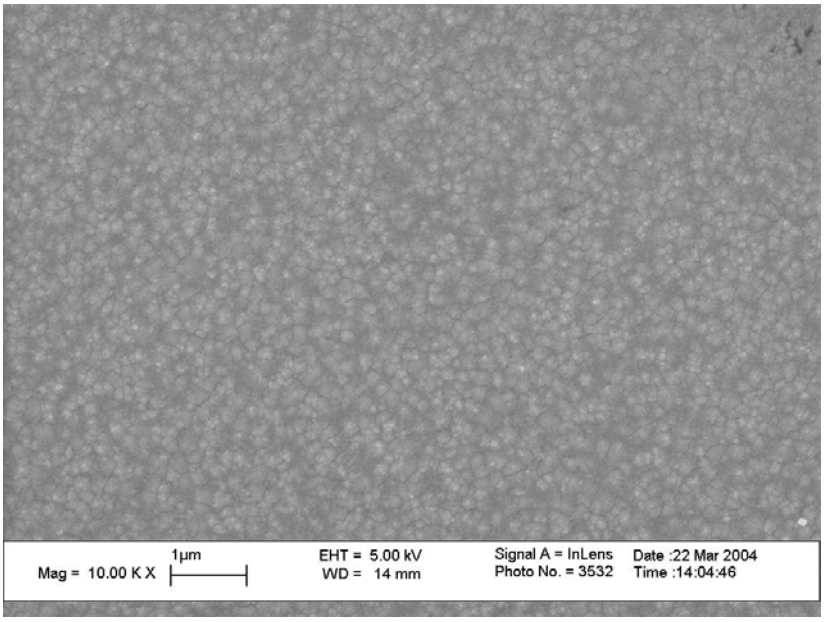



**Figure 6.4.A**. SEM picture of film from experiment 1.




B

**Figure 6.4.B**. SEM picture of film from experiment 4.

**Conclusion**

Compounds **23**-**25** were found to be viable MOCVD precursors based on thermogravimetric analyses and were subsequently utilized, in conjunction with $Zr(O^tBu)_4$ in the fabrication of metal oxide thin films via the use of a low-pressure, hot-walled tube furnace reactor. The as-deposited films were analyzed by high resolution XPS and SEM. Initial results suggest the synthesized alkoxide-amides are adequate in delivering tin and titanium cations to the substrate surface. The precursor cocktail comprised of separate sources of compound **2** and $Zr(OBu^t)_4$ resulted in a film that contained an oxide material containing all three metals in the molar ratio, $Zr_{0.97}Sn_{0.12}Ti_{0.05}O_{3.33}$. Based on these results, further investigation into the use of

compounds **23**-**25** as precursors for ZTT and optimization of the deposition conditions is warranted.

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# CHAPTER 7

# CONCLUSIONS AND FUTURE WORK

The attempt to synthesize molecular precursors for use in the MOCVD of ZTT has led to the isolation of a variety of coordination compounds possessing stannylamine ligands. Specifically, a series of dimeric beryllium and tetrameric silver amides, two series of Group 14-nitrogen heterocubanes, zinc and zirconium dimeric amido complexes, and a new class of heterometallic titanium alkoxides, all coordinated by stannylamine moieties were prepared and characterized.

The significance of the results reported herein lies on two fronts. First, the extension of the coordination chemistry of stannylamines, a field that has remained relatively unexplored, has been successfully carried out. Second, a novel route to volatile heterometallic alkoxide-amides containing tin(IV) cations was discovered.

Regarding the former case, the library of complexes possessing stannylamines was expanded in this work via the use of lithiated stannylamines. Amido transfer reagents of this nature were previously uncharacterized and limited in the synthesis of metal amides to the copper tetramer reported by Fenske and coworkers. Thus, the synthetic work reported in this dissertation has described the isolation and full characterization of lithiated stannylamines and documented initial reactions of these complexes with selected main group and transition metal halides. Future work in this area would lie primarily in synthesis. It would be of general interest from an inorganic synthetic chemistry standpoint to explore the reactions of the lithiated stannylamines reported in this dissertation with the full gamut of metals found in the periodic table and

compare the properties of the resulting complexes with any analogous alkyl- and silylamide congeners.

In regards to the latter case, tin-titanium alkoxide-amides were synthesized via the the reaction of lithiated stannylamines with tris(alkoxide) titanium(IV)chloride species. Initial TGA studies revealed that these complexes exhibit the volatility and vapor phase integrity necessary for MOCVD applications. Therefore, these precursors were subsequently employed in tandem with $Zr(O^tBu)_4$ in preliminary MOCVD experiments and were found to be viable candidates for the deposition of ZTT. With respect to the goals of this dissertation, that is the design and synthesis of ZTT MOCVD precursors, and to application in the materials industry, the results reported in Chapter 6 are most important. Future research related to this work can be encompassed by two major areas. First, a materials chemistry project could be pursued with the aim of carefully characterizating the alkoxide-amide/ $Zr(O^tBu)_4$ precursor cocktail and optimizing the MOCVD conditions in the preparation of ZTT thin films. Comparison of the film properties with those obtained by Senzaki, *et al*. and Rees *et al*. would shed light on the ultimate utility of the alkoxide-amide species as ZTT precursors. Second, a synthetic chemistry project could be initiated to investigate the extension of the heterometallic alkoxide-amide synthesis to other mixed metal systems possessing tin(IV) cations. The successful completion of this undertaking would potentially provide a convenient route to a variety of heterometallic oxide materials and could have an impact on the industrial fabrication of tinoxide materials.

To conclude this dissertation, the library of known stannylamide coordination complexes has been substantially increased, and the route employed to obtain them may

provide access to an even larger library of such compounds. Additionally, the lithiated stannylamines reported here were used to synthesize novel heterometallic alkoxide-amides that were found to exhibit adequate volatility and vapor phase integrity fur use in MOCVD processes. This class of compounds may ultimately result in an improved precursor system for the deposition of ZTT films and the synthetic pathway used to procure these alkoxide-amides has the potential to lead to a variety of new heterometallic coordination complexes.

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# APPENDIX A

# CRYSTALLOGRAPHIC TABLES

**Table A.1**. Atomic Coordinates (x $10^4$) and Equivalent Isotropic Displacement Parameters (Å x $10^3$) for $C_{20}H_{52}N_2O_2Li_2Sn_4$ (**1**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Sn(1) | 3571(1) | -970(1) | -1025(1) | 58(1) |
| N(1) | 5000 | 0 | -1629(5) | 52(3) |
| C(1) | 3041(16) | 86(19) | -2(6) | 149(7) |
| C(2) | 4163(12) | -2440(40) | -897(9) | 229(15) |
| C(3) | 1800(13) | -1070(20) | -1700(10) | 157(9) |
| C(4) | 7950(20) | -2620(20) | -3110(9) | 182(11) |
| C(5) | 8870(20) | -3490(20) | -2850(11) | 147(7) |
| O(1) | 7179(7) | -2179(7) | -2500 | 100(4) |
| Li(1) | 5830(14) | -830(14) | -2500 | 51(5) |

**Table A.2**. Interatomic Distances (Å) and Angles (°) for $C_{20}H_{52}N_2O_2Li_2Sn_4$ (**1**).

| | | | |
|---|---|---|---|
| Sn(1)-C(2) | 1.59(3) | C(3)-Sn(1)-C(1) | 107.0(7) |
| Sn(1)-N(1) | 2.022(4) | C(2)-Sn(1)-Li(1)#1 | 123.8(7) |
| Sn(1)-C(3) | 2.129(16) | N(1)-Sn(1)-Li(1)#1 | 34.6(3) |
| Sn(1)-C(1) | 2.160(12) | C(3)-Sn(1)-Li(1)#1 | 73.9(4) |
| Sn(1)-Li(1)#1 | 3.223(5) | C(1)-Sn(1)-Li(1)#1 | 117.2(5) |
| N(1)-Li(1)#1 | 1.935(14) | Li(1)#1-N(1)-Li(1) | 74.1(10) |
| N(1)-Li(1) | 1.935(14) | Li(1)#1-N(1)-Sn(1)#1 | 121.22(15) |
| N(1)-Sn(1)#1 | 2.022(4) | Li(1)-N(1)-Sn(1)#1 | 109.0(2) |
| C(4)-C(5) | 1.34(2) | Li(1)#1-N(1)-Sn(1) | 109.0(2) |
| C(4)-O(1) | 1.396(13) | Li(1)-N(1)-Sn(1) | 121.22(15) |
| C(5)-C(5)#2 | 1.35(3) | Sn(1)#1-N(1)-Sn(1) | 116.1(4) |
| O(1)-C(4)#2 | 1.396(13) | C(5)-C(4)-O(1) | 108.1(15) |
| O(1)-Li(1) | 1.90(2) | C(4)-C(5)-C(5)#2 | 107.8(12) |
| Li(1)-N(1)#3 | 1.935(14) | C(4)-O(1)-C(4)#2 | 104.9(15) |
| Li(1)-Li(1)#1 | 2.33(4) | C(4)-O(1)-Li(1) | 127.5(7) |
| Li(1)-Sn(1)#1 | 3.223(5) | C(4)#2-O(1)-Li(1) | 127.5(7) |
| Li(1)-Sn(1)#3 | 3.223(5) | O(1)-Li(1)-N(1)#3 | 127.0(5) |
| C(2)-Sn(1)-N(1) | 104.7(7) | O(1)-Li(1)-N(1) | 127.0(5) |
| C(2)-Sn(1)-C(3) | 110.1(8) | N(1)#3-Li(1)-N(1) | 105.9(10) |
| N(1)-Sn(1)-C(3) | 107.7(4) | O(1)-Li(1)-Li(1)#1 | 180.0 |
| C(2)-Sn(1)-C(1) | 114.6(7) | N(1)#3-Li(1)-Li(1)#1 | 53.0(5) |
| N(1)-Sn(1)-C(1) | 120.6(5) | N(1)-Li(1)-Li(1)#1 | 53.0(5) |

| | | | |
|---|---|---|---|
| O(1)-Li(1)-Sn(1)#1 | 105.2(3) | Li(1)#1-Li(1)-Sn(1)#3 | 74.8(3) |
| N(1)#3-Li(1)-Sn(1)#1 | 119.3(7) | Sn(1)#1-Li(1)-Sn(1)#3 | 149.7(7) |
| N(1)-Li(1)-Sn(1)#1 | 36.38(7) | O(1)-Li(1)-Sn(1)#3 | 105.2(3) |
| Li(1)#1-Li(1)-Sn(1)#1 | 74.8(3) | N(1)#3-Li(1)-Sn(1)#3 | 36.38(7) |

**Table A.3**. Anisotropic displacement parameters ($Å^2$ x $10^3$) for $C_{20}H_{52}N_2O_2Li_2Sn_4$ (**1**).

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Sn(1) | 67(1) | 64(1) | 43(1) | 9(1) | 7(1) | 0(1) |
| N(1) | 61(7) | 66(7) | 28(4) | 0 | 0 | 27(5) |
| C(1) | 213(19) | 35(14) | 98(9) | -27(10) | 110(11) | -45(16) |
| C(2) | 31(6) | 550(40) | 103(11) | -128(19) | -21(7) | 45(15) |
| C(3) | 47(7) | 260(20) | 166(15) | 132(15) | 9(8) | -22(10) |
| C(4) | 200(20) | 210(20) | 128(13) | -35(14) | 46(14) | 173(18) |
| C(5) | 124(16) | 150(19) | 170(20) | 4(14) | 39(14) | 31(12) |
| O(1) | 99(6) | 99(6) | 103(9) | -6(6) | -6(6) | 58(8) |
| Li(1) | 55(8) | 55(8) | 43(9) | -14(7) | -14(7) | 18(10) |

**Table A.4**. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å $^2$ x $10^3$) for $C_{20}H_{52}N_2O_2Li_2Sn_4$ (**1**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 3515 | -296 | 411 | 223 |
| H(1B) | 2100 | 9 | 82 | 223 |
| H(1C) | 3276 | 1009 | -51 | 223 |
| H(2A) | 4242 | -2887 | -1369 | 343 |
| H(2B) | 3575 | -2937 | -579 | 343 |
| H(2C) | 5024 | -2378 | -668 | 343 |
| H(3A) | 1975 | -680 | -2180 | 236 |
| H(3B) | 1096 | -586 | -1459 | 236 |
| H(3C) | 1540 | -1981 | -1762 | 236 |
| H(4A) | 7392 | -3044 | -3474 | 218 |
| H(4B) | 8385 | -1875 | -3343 | 218 |
| H(5A) | 9734 | -3079 | -2833 | 176 |
| H(5B) | 8922 | -4255 | -3172 | 176 |

**Table A.5**. Atomic Coordinates (x $10^4$) and Equivalent Isotropic Displacement Parameters (Å x $10^3$) for $C_{20}H_{52}N_2O_2Li_2Si_2Sn_2$ (**2**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Sn(1) | 1413(1) | 4046(1) | 1050(1) | 44(1) |
| Si(1) | 1413(1) | 4046(1) | 1050(1) | 44(1) |
| N(1) | 0 | 5000 | 1595(3) | 51(1) |
| C(1) | 3075(8) | 3965(8) | 1703(4) | 94(2) |
| C(2) | 854(7) | 2165(9) | 767(5) | 102(3) |
| C(3) | 1951(7) | 5069(8) | 77(3) | 81(2) |
| C(4) | 2699(9) | 7950(10) | 1826(4) | 107(3) |
| C(5) | 3020(20) | 9275(14) | 1929(9) | 334(17) |
| Li(1) | 874(9) | 5874(9) | 2500 | 56(3) |
| O(1) | 2262(4) | 7262(4) | 2500 | 71(2) |

**Table A.6**. Interatomic Distances (Å) and Angles (°) for $C_{20}H_{52}N_2O_2Li_2Si_2Sn_2$ (**2**).

| | | | |
|---|---|---|---|
| Sn(1)-N(1) | 1.919(3) | Sn(1)#1-N(1)-Sn(1) | 120.8(3) |
| Sn(1)-Li(1) | 3.138(4) | Si(1)#1-N(1)-Li(1) | 119.50(11) |
| Sn(1)-Li(1)#1 | 3.374(6) | Sn(1)#1-N(1)-Li(1) | 119.50(11) |
| N(1)-Si(1)#1 | 1.919(3) | Sn(1)-N(1)-Li(1) | 106.91(15) |
| N(1)-Sn(1)#1 | 1.919(3) | Si(1)#1-N(1)-Li(1)#1 | 106.91(15) |
| N(1)-Li(1) | 1.987(9) | Sn(1)#1-N(1)-Li(1)#1 | 106.91(15) |
| N(1)-Li(1)#1 | 1.987(9) | Sn(1)-N(1)-Li(1)#1 | 119.50(11) |
| C(4)-C(5) | 1.346(14) | Li(1)-N(1)-Li(1)#1 | 75.0(6) |
| C(4)-O(1) | 1.418(7) | C(5)-C(4)-O(1) | 114.6(9) |
| Li(1)-O(1) | 1.921(14) | O(1)-Li(1)-N(1) | 127.5(3) |
| Li(1)-N(1)#2 | 1.987(9) | O(1)-Li(1)-N(1)#2 | 127.5(3) |
| Li(1)-Li(1)#1 | 2.42(3) | N(1)-Li(1)-N(1)#2 | 105.0(6) |
| Li(1)-Si(1)#2 | 3.138(4) | O(1)-Li(1)-Li(1)#1 | 180.0(7) |
| Li(1)-Sn(1)#2 | 3.138(4) | N(1)-Li(1)-Li(1)#1 | 52.5(3) |
| Li(1)-Sn(1)#1 | 3.374(6) | N(1)#2-Li(1)-Li(1)#1 | 52.5(3) |
| Li(1)-Sn(1)#3 | 3.374(6) | O(1)-Li(1)-Si(1)#2 | 106.5(2) |
| O(1)-C(4)#2 | 1.418(7) | N(1)-Li(1)-Si(1)#2 | 117.7(4) |
| N(1)-Sn(1)-Li(1) | 37.29(19) | N(1)#2-Li(1)-Si(1)#2 | 35.80(5) |
| N(1)-Sn(1)-Li(1)#1 | 30.84(15) | Li(1)#1-Li(1)-Si(1)#2 | 73.5(2) |
| Li(1)-Sn(1)-Li(1)#1 | 43.4(4) | O(1)-Li(1)-Sn(1)#2 | 106.5(2) |
| Si(1)#1-N(1)-Sn(1)#1 | 0.00(3) | N(1)-Li(1)-Sn(1)#2 | 117.7(4) |
| Si(1)#1-N(1)-Sn(1) | 120.8(3) | N(1)#2-Li(1)-Sn(1)#2 | 35.80(5) |

| | | | |
|---|---|---|---|
| Li(1)#1-Li(1)-Sn(1)#2 | 73.5(2) | Sn(1)#2-Li(1)-Sn(1)#1 | 102.7(2) |
| Si(1)#2-Li(1)-Sn(1)#2 | 0.000(14) | Sn(1)-Li(1)-Sn(1)#1 | 61.52(10) |
| O(1)-Li(1)-Sn(1) | 106.5(2) | O(1)-Li(1)-Sn(1)#3 | 116.92(19) |
| N(1)-Li(1)-Sn(1) | 35.80(5) | N(1)-Li(1)-Sn(1)#3 | 108.5(4) |
| N(1)#2-Li(1)-Sn(1) | 117.7(4) | N(1)#2-Li(1)-Sn(1)#3 | 29.67(4) |
| Li(1)#1-Li(1)-Sn(1) | 73.5(2) | Li(1)#1-Li(1)-Sn(1)#3 | 63.08(19) |
| Si(1)#2-Li(1)-Sn(1) | 146.9(4) | Si(1)#2-Li(1)-Sn(1)#3 | 61.52(10) |
| Sn(1)#2-Li(1)-Sn(1) | 146.9(4) | Sn(1)#2-Li(1)-Sn(1)#3 | 61.52(10) |
| O(1)-Li(1)-Sn(1)#1 | 116.92(19) | Sn(1)-Li(1)-Sn(1)#3 | 102.7(2) |
| N(1)-Li(1)-Sn(1)#1 | 29.67(4) | Sn(1)#1-Li(1)-Sn(1)#3 | 126.2(4) |
| N(1)#2-Li(1)-Sn(1)#1 | 108.5(4) | C(4)#2-O(1)-C(4) | 113.5(7) |
| Li(1)#1-Li(1)-Sn(1)#1 | 63.08(19) | C(4)#2-O(1)-Li(1) | 123.3(3) |
| Si(1)#2-Li(1)-Sn(1)#1 | 102.7(2) | C(4)-O(1)-Li(1) | 123.3(3) |

**Table A.7**. Anisotropic displacement parameters ($Å^2$ x $10^3$) for $C_{20}H_{52}N_2O_2Li_2Si_2Sn_2$ (**2**).

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Sn(1) | 44(1) | 51(1) | 36(1) | -6(1) | 5(1) | 1(1) |
| Si(1) | 44(1) | 51(1) | 36(1) | -6(1) | 5(1) | 1(1) |
| N(1) | 41(3) | 48(3) | 64(4) | 0 | 0 | 4(2) |
| C(1) | 99(5) | 118(6) | 65(4) | -17(4) | 5(4) | -16(4) |
| C(2) | 73(5) | 124(7) | 109(6) | -42(5) | 13(4) | 1(4) |
| C(3) | 89(5) | 91(5) | 63(3) | 2(3) | 26(3) | 2(4) |
| C(4) | 103(6) | 141(7) | 75(4) | 19(5) | 0(4) | -63(5) |
| C(5) | 630(40) | 119(10) | 253(18) | -70(12) | 290(20) | -148(18) |
| Li(1) | 51(4) | 51(4) | 66(8) | -5(4) | 5(4) | 1(5) |
| O(1) | 74(2) | 74(2) | 63(3) | -8(2) | 8(2) | -26(3) |

**Table A.8**. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å $^2$ x $10^3$) for $C_{20}H_{52}N_2O_2Li_2Si_2Sn_2$ (**2**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 3355 | 4866 | 1831 | 190(30) |
| H(1B) | 3786 | 3517 | 1430 | 190(30) |
| H(1C) | 2878 | 3473 | 2160 | 190(30) |
| H(2A) | 440 | 1735 | 1198 | 140(20) |
| H(2B) | 1635 | 1658 | 614 | 140(20) |
| H(2C) | 219 | 2201 | 355 | 140(20) |
| H(3A) | 1188 | 5119 | -259 | 136(18) |
| H(3B) | 2677 | 4599 | -171 | 136(18) |
| H(3C) | 2240 | 5966 | 207 | 136(18) |
| H(4A) | 3476 | 7490 | 1627 | 620(120) |
| H(4B) | 1994 | 7890 | 1452 | 620(120) |
| H(5A) | 2451 | 9825 | 1611 | 550(110) |
| H(5B) | 3948 | 9419 | 1797 | 550(110) |
| H(5C) | 2878 | 9515 | 2452 | 550(110) |

**Table A.9**. Atomic Coordinates (x $10^4$) and Equivalent Isotropic Displacement Parameters (Å x $10^3$) for $C_{20}H_{56}N_2O_2Li_2Ge_2Sn_2$ (**3**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Ge(1) | 5916(1) | 1383(1) | 8964(1) | 37(1) |
| Sn(1) | 5916(1) | 1383(1) | 8964(1) | 37(1) |
| N(1) | 5000 | 0 | 8388(3) | 31(1) |
| C(1) | 6061(7) | 3077(7) | 8309(4) | 59(2) |
| C(2) | 4897(8) | 1960(7) | 9928(3) | 60(2) |
| C(3) | 7827(8) | 819(7) | 9255(4) | 68(2) |
| C(4) | 2131(7) | 2787(7) | 8171(4) | 62(2) |
| C(5) | 651(10) | 2673(16) | 8184(7) | 135(5) |
| O(1) | 2725(3) | 2275(3) | 7500 | 43(1) |
| Li(1) | 4126(8) | 874(8) | 7500 | 31(2) |

**Table A.10**. Interatomic Distances (Å) and Angles (°) for $C_{20}H_{52}N_2O_2Li_2Ge_2Sn_2$ (**3**).

| | | | |
|---|---|---|---|
| Ge(1)-N(1) | 1.915(3) | N(1)-Ge(1)-C(2) | 114.1(2) |
| Ge(1)-C(3) | 2.015(8) | C(3)-Ge(1)-C(2) | 108.3(3) |
| Ge(1)-C(1) | 2.026(6) | C(1)-Ge(1)-C(2) | 106.4(3) |
| Ge(1)-C(2) | 2.051(6) | N(1)-Ge(1)-Li(1) | 36.42(16) |
| Ge(1)-Li(1) | 3.162(3) | C(3)-Ge(1)-Li(1) | 132.7(3) |
| N(1)-Sn(1)#1 | 1.915(3) | C(1)-Ge(1)-Li(1) | 72.6(2) |
| N(1)-Ge(1)#1 | 1.915(3) | C(2)-Ge(1)-Li(1) | 116.9(3) |
| N(1)-Li(1) | 1.980(8) | Ge(1)-N(1)-Sn(1)#1 | 115.8(3) |
| N(1)-Li(1)#1 | 1.980(8) | Ge(1)-N(1)-Ge(1)#1 | 115.8(3) |
| C(4)-O(1) | 1.412(7) | Sn(1)#1-N(1)-Ge(1)#1 | 0.00(3) |
| C(4)-C(5) | 1.451(12) | Ge(1)-N(1)-Li(1) | 108.54(13) |
| O(1)-C(4)#2 | 1.412(7) | Sn(1)#1-N(1)-Li(1) | 121.61(9) |
| O(1)-Li(1) | 1.937(12) | Ge(1)#1-N(1)-Li(1) | 121.61(9) |
| Li(1)-N(1)#3 | 1.980(8) | Ge(1)-N(1)-Li(1)#1 | 121.61(9) |
| Li(1)-Li(1)#1 | 2.42(2) | Sn(1)#1-N(1)-Li(1)#1 | 108.54(13) |
| Li(1)-Sn(1)#2 | 3.162(3) | Ge(1)#1-N(1)-Li(1)#1 | 108.54(13) |
| Li(1)-Ge(1)#2 | 3.162(3) | Li(1)-N(1)-Li(1)#1 | 75.3(5) |
| Li(1)-Sn(1)#3 | 3.401(5) | O(1)-C(4)-C(5) | 113.4(7) |
| Li(1)-Sn(1)#1 | 3.401(5) | C(4)#2-O(1)-C(4) | 114.4(6) |
| N(1)-Ge(1)-C(3) | 112.07(19) | C(4)#2-O(1)-Li(1) | 122.8(3) |
| N(1)-Ge(1)-C(1) | 107.9(2) | C(4)-O(1)-Li(1) | 122.8(3) |
| C(3)-Ge(1)-C(1) | 107.7(3) | O(1)-Li(1)-N(1)#3 | 127.6(3) |

| | | | |
|---|---|---|---|
| O(1)-Li(1)-N(1) | 127.6(3) | Sn(1)#2-Li(1)-Ge(1) | 147.5(4) |
| N(1)#3-Li(1)-N(1) | 104.7(5) | Ge(1)#2-Li(1)-Ge(1) | 147.5(4) |
| O(1)-Li(1)-Li(1)#1 | 180.0(6) | O(1)-Li(1)-Sn(1)#3 | 116.79(16) |
| N(1)#3-Li(1)-Li(1)#1 | 52.4(3) | N(1)#3-Li(1)-Sn(1)#3 | 28.66(3) |
| N(1)-Li(1)-Li(1)#1 | 52.4(3) | N(1)-Li(1)-Sn(1)#3 | 109.1(4) |
| O(1)-Li(1)-Sn(1)#2 | 106.27(18) | Li(1)#1-Li(1)-Sn(1)#3 | 63.21(16) |
| N(1)#3-Li(1)-Sn(1)#2 | 35.04(5) | Sn(1)#2-Li(1)-Sn(1)#3 | 59.11(8) |
| N(1)-Li(1)-Sn(1)#2 | 118.5(4) | Ge(1)#2-Li(1)-Sn(1)#3 | 59.11(8) |
| Li(1)#1-Li(1)-Sn(1)#2 | 73.73(18) | Ge(1)-Li(1)-Sn(1)#3 | 105.12(18) |
| O(1)-Li(1)-Ge(1)#2 | 106.27(18) | O(1)-Li(1)-Sn(1)#1 | 116.79(16) |
| N(1)#3-Li(1)-Ge(1)#2 | 35.04(5) | N(1)#3-Li(1)-Sn(1)#1 | 109.1(4) |
| N(1)-Li(1)-Ge(1)#2 | 118.5(4) | N(1)-Li(1)-Sn(1)#1 | 28.66(3) |
| Li(1)#1-Li(1)-Ge(1)#2 | 73.73(18) | Li(1)#1-Li(1)-Sn(1)#1 | 63.21(16) |
| Sn(1)#2-Li(1)-Ge(1)#2 | 0.000(18) | Sn(1)#2-Li(1)-Sn(1)#1 | 105.12(18) |
| O(1)-Li(1)-Ge(1) | 106.27(18) | Ge(1)#2-Li(1)-Sn(1)#1 | 105.12(18) |
| N(1)#3-Li(1)-Ge(1) | 118.5(4) | Ge(1)-Li(1)-Sn(1)#1 | 59.11(8) |
| N(1)-Li(1)-Ge(1) | 35.04(5) | Sn(1)#3-Li(1)-Sn(1)#1 | 126.4(3) |
| Li(1)#1-Li(1)-Ge(1) | 73.73(18) | | |

**Table A.11**. Anisotropic displacement parameters ($Å^2$ x $10^3$) for $C_{20}H_{52}N_2O_2Li_2Ge_2Sn_2$ (**3**).

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Ge(1) | 46(1) | 34(1) | 31(1) | -3(1) | -2(1) | -3(1) |
| Sn(1) | 46(1) | 34(1) | 31(1) | -3(1) | -2(1) | -3(1) |
| N(1) | 35(3) | 34(3) | 24(2) | 0 | 0 | -6(2) |
| C(1) | 78(4) | 47(3) | 53(4) | 5(3) | -2(3) | -9(3) |
| C(2) | 69(4) | 64(4) | 49(3) | -22(3) | 10(3) | -6(4) |
| C(3) | 76(5) | 59(4) | 68(4) | -6(3) | -20(4) | -4(3) |
| C(4) | 67(4) | 65(4) | 54(4) | -10(3) | 10(3) | 14(3) |
| C(5) | 93(7) | 178(12) | 135(10) | -71(10) | 6(7) | 5(7) |
| O(1) | 47(2) | 47(2) | 34(3) | 1(2) | 1(2) | 11(2) |
| Li(1) | 32(3) | 32(3) | 29(5) | -10(3) | -10(3) | 5(4) |

**Table A.12**. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å $^2$ x $10^3$) for $C_{20}H_{52}N_2O_2Li_2Ge_2Sn_2$ (**3**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 5247 | 3601 | 8355 | 160(30) |
| H(1B) | 6184 | 2815 | 7796 | 160(30) |
| H(1C) | 6820 | 3610 | 8469 | 160(30) |
| H(2A) | 4937 | 1241 | 10289 | 114(19) |
| H(2B) | 3969 | 2151 | 9808 | 114(19) |
| H(2C) | 5313 | 2756 | 10132 | 114(19) |
| H(3A) | 8323 | 573 | 8813 | 100(18) |
| H(3B) | 7786 | 59 | 9589 | 100(18) |
| H(3C) | 8273 | 1560 | 9500 | 100(18) |
| H(4A) | 2376 | 3722 | 8226 | 190(40) |
| H(4B) | 2496 | 2303 | 8591 | 190(40) |
| H(5A) | 391 | 1774 | 8040 | 250(50) |
| H(5B) | 267 | 3314 | 7840 | 250(50) |
| H(5C) | 327 | 2856 | 8681 | 250(50) |

**Table A.13**. Atomic Coordinates (x $10^4$) and Equivalent Isotropic Displacement Parameters (Å x $10^3$) for $C_{20}H_{52}N_2O_2Cl_2Be_2Sn_4$ (**4**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Sn(1) | 5101(1) | 222(1) | 2371(1) | 31(1) |
| Sn(2) | 7648(1) | 104(1) | 4804(1) | 29(1) |
| Cl(1) | 3437(2) | -1422(1) | 3346(2) | 31(1) |
| N(1) | 5704(5) | 91(4) | 4271(5) | 21(1) |
| O(1) | 4320(5) | 1884(4) | 4585(5) | 32(1) |
| Be(1) | 5144(7) | 815(6) | 5231(8) | 23(2) |
| C(1) | 6287(9) | 1321(8) | 1857(9) | 48(2) |
| C(2) | 5279(10) | -1183(7) | 1488(9) | 51(2) |
| C(3) | 3274(8) | 793(8) | 1525(8) | 45(2) |
| C(4) | 8543(8) | -688(8) | 6454(9) | 49(2) |
| C(5) | 8434(8) | 1611(7) | 4906(9) | 41(2) |
| C(6) | 8260(8) | -670(8) | 3433(10) | 49(2) |
| C(7) | 4893(8) | 2609(6) | 3963(8) | 40(2) |
| C(8) | 4812(11) | 3622(8) | 4467(13) | 65(3) |
| C(9) | 4073(17) | 3526(9) | 5271(15) | 91(5) |
| C(10) | 3705(9) | 2478(7) | 5299(11) | 53(3) |

**Table A.14**. Interatomic Distances (Å) and Angles (°) for $C_{20}H_{52}N_2O_2Cl_2Be_2Sn_4$ (**4**).

| | | | |
|---|---|---|---|
| Sn(1)-N(1) | 2.092(6) | C(3)-Sn(1)-C(2) | 107.5(4) |
| Sn(1)-C(3) | 2.132(9) | N(1)-Sn(1)-C(1) | 107.9(3) |
| Sn(1)-C(2) | 2.136(9) | C(3)-Sn(1)-C(1) | 103.7(4) |
| Sn(1)-C(1) | 2.166(9) | C(2)-Sn(1)-C(1) | 106.5(4) |
| Sn(2)-N(1) | 2.094(5) | N(1)-Sn(2)-C(4) | 115.5(3) |
| Sn(2)-C(4) | 2.130(9) | N(1)-Sn(2)-C(5) | 113.8(3) |
| Sn(2)-C(5) | 2.148(8) | C(4)-Sn(2)-C(5) | 108.6(4) |
| Sn(2)-C(6) | 2.157(9) | N(1)-Sn(2)-C(6) | 108.8(3) |
| Cl(1)-Be(1)#1 | 2.072(9) | C(4)-Sn(2)-C(6) | 104.7(4) |
| N(1)-Be(1) | 1.715(10) | C(5)-Sn(2)-C(6) | 104.5(4) |
| N(1)-Be(1)#1 | 1.726(10) | Be(1)-N(1)-Be(1)#1 | 79.3(5) |
| O(1)-C(10) | 1.452(10) | Be(1)-N(1)-Sn(1) | 124.2(4) |
| O(1)-C(7) | 1.452(9) | Be(1)#1-N(1)-Sn(1) | 111.4(4) |
| O(1)-Be(1) | 1.718(10) | Be(1)-N(1)-Sn(2) | 111.4(4) |
| Be(1)-N(1)#1 | 1.726(10) | Be(1)#1-N(1)-Sn(2) | 123.2(4) |
| Be(1)-Cl(1)#1 | 2.072(9) | Sn(1)-N(1)-Sn(2) | 106.7(2) |
| Be(1)-Be(1)#1 | 2.195(17) | C(10)-O(1)-C(7) | 106.9(6) |
| C(7)-C(8) | 1.459(13) | C(10)-O(1)-Be(1) | 118.6(6) |
| C(8)-C(9) | 1.427(17) | C(7)-O(1)-Be(1) | 118.7(5) |
| C(9)-C(10) | 1.434(13) | N(1)-Be(1)-O(1) | 115.2(6) |
| N(1)-Sn(1)-C(3) | 118.0(3) | N(1)-Be(1)-N(1)#1 | 100.7(5) |
| N(1)-Sn(1)-C(2) | 112.3(3) | O(1)-Be(1)-N(1)#1 | 114.7(5) |

| | | | |
|---|---|---|---|
| N(1)-Be(1)-Cl(1)#1 | 111.9(4) | Cl(1)#1-Be(1)-Be(1)#1 | 125.8(6) |
| O(1)-Be(1)-Cl(1)#1 | 102.7(5) | O(1)-C(7)-C(8) | 107.8(8) |
| N(1)#1-Be(1)-Cl(1)#1 | 112.0(5) | C(9)-C(8)-C(7) | 107.3(9) |
| N(1)-Be(1)-Be(1)#1 | 50.6(4) | C(8)-C(9)-C(10) | 109.2(9) |
| O(1)-Be(1)-Be(1)#1 | 131.5(7) | C(9)-C(10)-O(1) | 107.8(8) |
| N(1)#1-Be(1)-Be(1)#1 | 50.2(4) | | |

**Table A.15**. Anisotropic displacement parameters ($Å^2$ x $10^3$) for $C_{20}H_{52}N_2O_2Cl_2Be_2Sn_4$ (**4**).

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Sn(1) | 38(1) | 30(1) | 27(1) | -1(1) | 15(1) | -4(1) |
| Sn(2) | 24(1) | 24(1) | 43(1) | 0(1) | 15(1) | -2(1) |
| Cl(1) | 31(1) | 29(1) | 33(1) | -5(1) | 9(1) | -8(1) |
| N(1) | 17(2) | 21(3) | 26(2) | 3(2) | 7(2) | 1(2) |
| O(1) | 29(3) | 23(3) | 46(3) | 2(2) | 15(2) | 1(2) |
| Be(1) | 21(4) | 15(4) | 35(4) | 3(3) | 11(3) | -2(3) |
| C(1) | 58(6) | 51(6) | 46(5) | 11(4) | 34(4) | -4(4) |
| C(2) | 71(6) | 39(5) | 48(5) | -17(4) | 27(5) | -2(4) |
| C(3) | 47(5) | 44(5) | 41(4) | 7(4) | 7(4) | 1(4) |
| C(4) | 37(4) | 45(5) | 64(6) | 16(4) | 15(4) | 9(4) |
| C(5) | 37(4) | 31(4) | 60(5) | -5(4) | 22(4) | -13(3) |
| C(6) | 35(4) | 48(5) | 71(6) | -17(5) | 26(4) | -2(4) |
| C(7) | 52(5) | 24(4) | 49(5) | 9(3) | 22(4) | 2(3) |
| C(8) | 79(8) | 24(5) | 107(9) | -4(5) | 53(7) | -9(4) |
| C(9) | 161(14) | 27(5) | 124(12) | -24(6) | 103(12) | -20(7) |
| C(10) | 56(6) | 23(4) | 96(8) | 1(4) | 49(6) | 4(4) |

**Table A.16**. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å $^2$ x $10^3$) for $C_{20}H_{52}N_2O_2Cl_2Be_2Sn_4$ (**4**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 6715 | 1718 | 2548 | 120(30) |
| H(1B) | 5796 | 1758 | 1238 | 120(30) |
| H(1C) | 6872 | 969 | 1559 | 120(30) |
| H(2A) | 5625 | -1690 | 2085 | 140(40) |
| H(2B) | 5807 | -1083 | 994 | 140(40) |
| H(2C) | 4484 | -1399 | 993 | 140(40) |
| H(3A) | 2683 | 333 | 1671 | 56(18) |
| H(3B) | 3138 | 855 | 673 | 56(18) |
| H(3C) | 3188 | 1445 | 1856 | 56(18) |
| H(4A) | 8763 | -215 | 7111 | 100(30) |
| H(4B) | 9270 | -1015 | 6386 | 100(30) |
| H(4C) | 7994 | -1187 | 6601 | 100(30) |
| H(5A) | 7793 | 2092 | 4561 | 190(60) |
| H(5B) | 9024 | 1625 | 4468 | 190(60) |
| H(5C) | 8832 | 1782 | 5735 | 190(60) |
| H(6A) | 7998 | -1364 | 3378 | 60(19) |
| H(6B) | 9140 | -643 | 3649 | 60(19) |
| H(6C) | 7911 | -344 | 2668 | 60(19) |
| H(7A) | 4472 | 2603 | 3113 | 60(20) |
| H(7B) | 5736 | 2431 | 4084 | 60(20) |
| H(8A) | 5618 | 3865 | 4898 | 150(60) |

| | | | | |
|---|---|---|---|---|
| H(8B) | 4440 | 4092 | 3831 | 150(60) |
| H(9A) | 3358 | 3949 | 4997 | 180(70) |
| H(9B) | 4537 | 3742 | 6066 | 180(70) |
| H(10A) | 2830 | 2417 | 4965 | 70(20) |
| H(10B) | 3940 | 2236 | 6115 | 70(20) |

**Table A.17**. Atomic Coordinates (x $10^4$) and Equivalent Isotropic Displacement Parameters (Å x $10^3$) for $C_{14}H_{36}Be_2F_6N_2O_6S_2Sn_4$ (**5**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Sn(1) | 4126(1) | 8849(1) | 841(1) | 32(1) |
| Sn(2) | 3030(1) | 10547(1) | 1622(1) | 38(1) |
| Sn(3) | 1133(1) | 11474(1) | -1287(1) | 38(1) |
| Sn(4) | 1912(1) | 9001(1) | -1959(1) | 33(1) |
| S(1) | 3510(1) | 12711(1) | -816(1) | 34(1) |
| S(2) | 1747(1) | 7152(1) | 536(1) | 47(1) |
| Be(1) | 2864(3) | 10677(6) | -254(3) | 29(1) |
| Be(2) | 2208(4) | 9227(6) | -117(4) | 32(1) |
| N(1) | 3053(2) | 9766(4) | 555(2) | 29(1) |
| N(2) | 2025(2) | 10115(4) | -935(2) | 29(1) |
| O(1) | 3413(2) | 11734(3) | -276(2) | 39(1) |
| O(2) | 2795(2) | 13143(4) | -1450(2) | 54(1) |
| O(3) | 4119(2) | 12398(4) | -1027(2) | 51(1) |
| O(4) | 1643(2) | 8238(4) | -48(2) | 45(1) |
| O(5) | 2266(3) | 6184(5) | 509(3) | 73(1) |
| O(6) | 1805(3) | 7571(4) | 1304(2) | 60(1) |
| C(1) | 3885(3) | 14010(5) | -68(3) | 43(1) |
| C(2) | 809(4) | 6420(6) | -1(4) | 56(2) |
| C(3) | 4157(4) | 7014(5) | 1343(4) | 51(1) |
| C(4) | 4168(3) | 8742(6) | -320(3) | 47(1) |

| | | | | |
|---|---|---|---|---|
| C(5) | 5010(3) | 10055(5) | 1691(3) | 43(1) |
| C(6) | 3594(4) | 12345(6) | 1833(3) | 50(1) |
| C(7) | 1834(4) | 10747(7) | 1359(4) | 59(2) |
| C(8) | 3609(4) | 9224(6) | 2600(3) | 57(2) |
| C(9) | 1552(4) | 12939(5) | -372(4) | 56(2) |
| C(10) | 951(3) | 12220(6) | -2455(4) | 53(2) |
| C(11) | 157(3) | 10516(6) | -1279(5) | 61(2) |
| C(12) | 2594(3) | 9943(6) | -2457(3) | 48(1) |
| C(13) | 699(3) | 8882(6) | -2793(4) | 54(2) |
| C(14) | 2260(4) | 7134(5) | -1487(4) | 60(2) |
| F(1) | 4525(2) | 13656(3) | 583(2) | 55(1) |
| F(2) | 3362(2) | 14364(3) | 180(2) | 66(1) |
| F(3) | 4053(2) | 14989(3) | -413(2) | 65(1) |
| F(4) | 690(2) | 6043(4) | -751(2) | 72(1) |
| F(5) | 804(3) | 5386(4) | 421(3) | 76(1) |
| F(6) | 249(2) | 7240(5) | -66(3) | 93(2) |

**Table A.18**. Interatomic Distances (Å) and Angles (°) for $C_{14}H_{36}Be_2F_6N_2O_6S_2Sn_4$ (**5**).

| | | | |
|---|---|---|---|
| Sn(1)-N(1) | 2.124(4) | S(2)-O(4) | 1.509(4) |
| Sn(1)-C(3) | 2.129(5) | S(2)-C(2) | 1.799(6) |
| Sn(1)-C(4) | 2.133(5) | Be(1)-O(1) | 1.549(7) |
| Sn(1)-C(5) | 2.135(5) | Be(1)-N(2) | 1.645(7) |
| Sn(2)-N(1) | 2.113(4) | Be(1)-N(1) | 1.649(7) |
| Sn(2)-C(6) | 2.136(6) | Be(1)-Be(2) | 2.067(9) |
| Sn(2)-C(8) | 2.137(6) | Be(2)-O(4) | 1.551(7) |
| Sn(2)-C(7) | 2.141(6) | Be(2)-N(1) | 1.639(7) |
| Sn(3)-N(2) | 2.107(4) | Be(2)-N(2) | 1.650(7) |
| Sn(3)-C(10) | 2.128(6) | C(1)-F(3) | 1.318(6) |
| Sn(3)-C(11) | 2.135(6) | C(1)-F(2) | 1.321(7) |
| Sn(3)-C(9) | 2.143(6) | C(1)-F(1) | 1.324(6) |
| Sn(4)-N(2) | 2.119(4) | C(2)-F(4) | 1.330(8) |
| Sn(4)-C(12) | 2.132(5) | C(2)-F(5) | 1.334(7) |
| Sn(4)-C(14) | 2.135(6) | C(2)-F(6) | 1.346(8) |
| Sn(4)-C(13) | 2.146(5) | N(1)-Sn(1)-C(3) | 111.1(2) |
| S(1)-O(3) | 1.419(4) | N(1)-Sn(1)-C(4) | 103.80(17) |
| S(1)-O(2) | 1.420(4) | C(3)-Sn(1)-C(4) | 111.3(2) |
| S(1)-O(1) | 1.487(4) | N(1)-Sn(1)-C(5) | 106.27(18) |
| S(1)-C(1) | 1.834(5) | C(3)-Sn(1)-C(5) | 112.0(2) |
| S(2)-O(6) | 1.412(4) | C(4)-Sn(1)-C(5) | 111.9(2) |
| S(2)-O(5) | 1.444(5) | N(1)-Sn(2)-C(6) | 107.27(18) |

| | | | |
|---|---|---|---|
| N(1)-Sn(2)-C(8) | 106.5(2) | O(6)-S(2)-O(5) | 120.0(3) |
| C(6)-Sn(2)-C(8) | 113.4(2) | O(6)-S(2)-O(4) | 112.0(3) |
| N(1)-Sn(2)-C(7) | 106.8(2) | O(5)-S(2)-O(4) | 113.3(3) |
| C(6)-Sn(2)-C(7) | 111.2(3) | O(6)-S(2)-C(2) | 106.8(3) |
| C(8)-Sn(2)-C(7) | 111.3(3) | O(5)-S(2)-C(2) | 102.7(3) |
| N(2)-Sn(3)-C(10) | 107.9(2) | O(4)-S(2)-C(2) | 99.1(3) |
| N(2)-Sn(3)-C(11) | 106.0(2) | O(1)-Be(1)-N(2) | 134.0(4) |
| C(10)-Sn(3)-C(11) | 114.9(3) | O(1)-Be(1)-N(1) | 123.9(4) |
| N(2)-Sn(3)-C(9) | 106.33(19) | N(2)-Be(1)-N(1) | 102.1(4) |
| C(10)-Sn(3)-C(9) | 109.6(3) | O(1)-Be(1)-Be(2) | 174.7(4) |
| C(11)-Sn(3)-C(9) | 111.7(3) | N(2)-Be(1)-Be(2) | 51.3(3) |
| N(2)-Sn(4)-C(12) | 105.17(18) | N(1)-Be(1)-Be(2) | 50.9(3) |
| N(2)-Sn(4)-C(14) | 105.81(19) | O(4)-Be(2)-N(1) | 132.4(4) |
| C(12)-Sn(4)-C(14) | 117.1(3) | O(4)-Be(2)-N(2) | 125.1(4) |
| N(2)-Sn(4)-C(13) | 107.75(19) | N(1)-Be(2)-N(2) | 102.3(4) |
| C(12)-Sn(4)-C(13) | 114.3(2) | O(4)-Be(2)-Be(1) | 173.9(5) |
| C(14)-Sn(4)-C(13) | 106.1(3) | N(1)-Be(2)-Be(1) | 51.3(3) |
| O(3)-S(1)-O(2) | 118.6(3) | N(2)-Be(2)-Be(1) | 51.0(3) |
| O(3)-S(1)-O(1) | 111.7(2) | Be(2)-N(1)-Be(1) | 77.9(3) |
| O(2)-S(1)-O(1) | 113.2(2) | Be(2)-N(1)-Sn(2) | 113.4(3) |
| O(3)-S(1)-C(1) | 105.7(3) | Be(1)-N(1)-Sn(2) | 119.5(3) |
| O(2)-S(1)-C(1) | 106.1(3) | Be(2)-N(1)-Sn(1) | 123.9(3) |
| O(1)-S(1)-C(1) | 99.2(2) | Be(1)-N(1)-Sn(1) | 107.0(3) |

| | | | |
|---|---|---|---|
| Sn(2)-N(1)-Sn(1) | 111.43(16) | F(3)-C(1)-S(1) | 109.8(4) |
| Be(1)-N(2)-Be(2) | 77.7(3) | F(2)-C(1)-S(1) | 110.5(4) |
| Be(1)-N(2)-Sn(3) | 112.2(3) | F(1)-C(1)-S(1) | 110.5(4) |
| Be(2)-N(2)-Sn(3) | 118.7(3) | F(4)-C(2)-F(5) | 107.1(5) |
| Be(1)-N(2)-Sn(4) | 122.7(3) | F(4)-C(2)-F(6) | 109.4(5) |
| Be(2)-N(2)-Sn(4) | 111.2(3) | F(5)-C(2)-F(6) | 111.8(6) |
| Sn(3)-N(2)-Sn(4) | 111.04(16) | F(4)-C(2)-S(2) | 110.9(4) |
| S(1)-O(1)-Be(1) | 143.3(3) | F(5)-C(2)-S(2) | 107.6(4) |
| S(2)-O(4)-Be(2) | 133.3(3) | F(6)-C(2)-S(2) | 110.0(5) |
| F(3)-C(1)-F(2) | 108.6(5) | F(2)-C(1)-F(1) | 109.0(5) |

**Table A.19**. Anisotropic displacement parameters ($Å^2$ x $10^3$) for $C_{14}H_{36}Be_2F_6N_2O_6S_2Sn_4$ (**5**).

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Sn(1) | 33(1) | 35(1) | 26(1) | -1(1) | 11(1) | 2(1) |
| Sn(2) | 44(1) | 44(1) | 31(1) | -8(1) | 22(1) | -6(1) |
| Sn(3) | 29(1) | 37(1) | 47(1) | 4(1) | 18(1) | 5(1) |
| Sn(4) | 31(1) | 40(1) | 29(1) | -4(1) | 15(1) | -4(1) |
| S(1) | 34(1) | 36(1) | 31(1) | 1(1) | 12(1) | -5(1) |
| S(2) | 46(1) | 51(1) | 41(1) | 3(1) | 17(1) | -15(1) |
| Be(1) | 31(3) | 34(3) | 24(2) | -3(2) | 15(2) | 1(2) |
| Be(2) | 34(3) | 34(3) | 30(3) | -1(2) | 16(2) | 0(2) |
| N(1) | 30(2) | 35(2) | 26(2) | -2(2) | 16(2) | 0(2) |
| N(2) | 28(2) | 33(2) | 29(2) | 1(2) | 15(2) | 3(2) |
| O(1) | 40(2) | 42(2) | 35(2) | -1(2) | 15(2) | -13(2) |
| O(2) | 43(2) | 53(2) | 43(2) | 4(2) | -2(2) | -1(2) |
| O(3) | 53(2) | 64(3) | 47(2) | -3(2) | 31(2) | -5(2) |
| O(4) | 44(2) | 47(2) | 44(2) | 5(2) | 19(2) | -11(2) |
| O(5) | 58(3) | 87(3) | 88(3) | 39(3) | 45(3) | 33(3) |
| O(6) | 86(3) | 54(2) | 37(2) | -7(2) | 25(2) | -13(2) |
| C(1) | 47(3) | 41(3) | 38(3) | 1(2) | 18(2) | -10(2) |
| C(2) | 47(3) | 61(4) | 60(4) | -2(3) | 23(3) | -13(3) |
| C(3) | 52(3) | 42(3) | 53(3) | 7(3) | 18(3) | 5(3) |
| C(4) | 37(3) | 69(4) | 34(2) | -2(2) | 15(2) | 6(3) |
| C(5) | 35(3) | 54(3) | 40(3) | -8(2) | 18(2) | -3(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(6) | 62(4) | 51(3) | 44(3) | -14(3) | 30(3) | -8(3) |
| C(7) | 56(4) | 69(4) | 70(4) | -14(3) | 43(3) | -4(3) |
| C(8) | 75(4) | 68(4) | 32(3) | 0(3) | 27(3) | -8(3) |
| C(9) | 54(4) | 42(3) | 77(4) | -12(3) | 35(3) | 5(3) |
| C(10) | 45(3) | 54(3) | 53(3) | 18(3) | 15(3) | 3(3) |
| C(11) | 40(3) | 61(4) | 99(5) | 7(4) | 45(3) | 2(3) |
| C(12) | 43(3) | 73(4) | 35(2) | -11(3) | 24(2) | -18(3) |
| C(13) | 33(3) | 76(4) | 50(3) | -20(3) | 17(2) | -15(3) |
| C(14) | 86(5) | 42(3) | 62(4) | -3(3) | 43(3) | 9(3) |
| F(1) | 49(2) | 62(2) | 39(2) | -1(2) | 8(1) | -16(2) |
| F(2) | 71(2) | 56(2) | 78(2) | -23(2) | 41(2) | -7(2) |
| F(3) | 87(3) | 45(2) | 57(2) | 6(2) | 25(2) | -23(2) |
| F(4) | 75(3) | 73(3) | 47(2) | -17(2) | 7(2) | -21(2) |
| F(5) | 91(3) | 53(2) | 88(3) | 2(2) | 44(2) | -32(2) |
| F(6) | 51(2) | 102(4) | 134(4) | 11(3) | 50(3) | 15(2) |

**Table A.20**. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å $^2$ x $10^3$) for $C_{14}H_{36}Be_2F_6N_2O_6S_2Sn_4$ (**5**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(3A) | 4287 | 7085 | 1914 | 77(13) |
| H(3B) | 4536 | 6512 | 1276 | 77(13) |
| H(3C) | 3662 | 6626 | 1062 | 77(13) |
| H(4A) | 3807 | 8126 | -658 | 88(15) |
| H(4B) | 4676 | 8511 | -233 | 88(15) |
| H(4C) | 4039 | 9544 | -585 | 88(15) |
| H(5A) | 4921 | 10899 | 1488 | 73(13) |
| H(5B) | 5503 | 9778 | 1751 | 73(13) |
| H(5C) | 4999 | 10026 | 2213 | 73(13) |
| H(6A) | 3973 | 12332 | 1630 | 104(17) |
| H(6B) | 3838 | 12519 | 2410 | 104(17) |
| H(6C) | 3221 | 12984 | 1555 | 104(17) |
| H(7A) | 1518 | 10619 | 785 | 140(20) |
| H(7B) | 1747 | 11574 | 1509 | 140(20) |
| H(7C) | 1705 | 10138 | 1667 | 140(20) |
| H(8A) | 3440 | 8391 | 2405 | 93(15) |
| H(8B) | 3490 | 9408 | 3047 | 93(15) |
| H(8C) | 4153 | 9284 | 2782 | 93(15) |
| H(9A) | 2089 | 12813 | -27 | 109(18) |
| H(9B) | 1275 | 12914 | -47 | 109(18) |
| H(9C) | 1477 | 13738 | -637 | 109(18) |

| | | | | |
|---|---|---|---|---|
| H(10A) | 1297 | 11824 | -2630 | 78(13) |
| H(10B) | 1044 | 13106 | -2407 | 78(13) |
| H(10C) | 431 | 12063 | -2849 | 78(13) |
| H(11A) | -249 | 10476 | -1826 | 120(20) |
| H(11B) | -19 | 10964 | -937 | 120(20) |
| H(11C) | 304 | 9683 | -1071 | 120(20) |
| H(12A) | 2721 | 10768 | -2228 | 116(19) |
| H(12B) | 2307 | 10001 | -3040 | 116(19) |
| H(12C) | 3057 | 9477 | -2324 | 116(19) |
| H(13A) | 414 | 8691 | -2490 | 93(15) |
| H(13B) | 619 | 8234 | -3187 | 93(15) |
| H(13C) | 527 | 9668 | -3069 | 93(15) |
| H(14A) | 2721 | 7177 | -982 | 101(17) |
| H(14B) | 2356 | 6649 | -1877 | 101(17) |
| H(14C) | 1860 | 6747 | -1394 | 101(17) |

**Table A.21**. Atomic Coordinates (x $10^4$) and Equivalent Isotropic Displacement Parameters (Å x $10^3$) for $C_{14}H_{36}N_2O_2Cl_2Be_2Si_2$ (**6**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Cl(1) | 9804(1) | 2564(1) | 810(1) | 41(1) |
| Si(1) | 12064(1) | 231(1) | 1108(1) | 35(1) |
| N(1) | 12373(3) | 1444(3) | 562(2) | 30(1) |
| O(1) | 11992(2) | 3872(2) | 545(1) | 35(1) |
| Be(1) | 11405(4) | 2536(4) | 336(3) | 31(1) |
| C(1) | 13384(4) | -761(4) | 1144(3) | 53(1) |
| C(2) | 10779(4) | -624(4) | 784(2) | 47(1) |
| C(3) | 11760(5) | 737(4) | 2031(2) | 53(1) |
| C(4) | 11472(5) | 4919(4) | 242(2) | 46(1) |
| C(5) | 11762(5) | 5904(4) | 750(3) | 62(2) |
| C(6) | 11918(7) | 5288(5) | 1448(4) | 85(2) |
| C(7) | 12338(5) | 4106(4) | 1282(2) | 53(1) |

**Table A.22**. Interatomic Distances (Å) and Angles (°) for $C_{14}H_{36}N_2O_2Cl_2Be_2Si_2$ (**6**).

| | | | |
|---|---|---|---|
| Cl(1)-Be(1) | 2.026(5) | Be(1)#1-N(1)-Si(1) | 125.8(2) |
| Si(1)-N(1) | 1.756(3) | Be(1)-N(1)-Si(1) | 125.9(2) |
| Si(1)-C(2) | 1.856(5) | C(4)-O(1)-C(7) | 109.6(3) |
| Si(1)-C(3) | 1.865(4) | C(4)-O(1)-Be(1) | 118.8(3) |
| Si(1)-C(1) | 1.876(5) | C(7)-O(1)-Be(1) | 119.0(3) |
| N(1)-Be(1)#1 | 1.704(6) | O(1)-Be(1)-N(1)#1 | 108.5(3) |
| N(1)-Be(1) | 1.711(6) | O(1)-Be(1)-N(1) | 109.7(3) |
| O(1)-C(4) | 1.445(5) | N(1)#1-Be(1)-N(1) | 98.7(3) |
| O(1)-C(7) | 1.470(5) | O(1)-Be(1)-Cl(1) | 103.6(3) |
| O(1)-Be(1) | 1.703(5) | N(1)#1-Be(1)-Cl(1) | 117.6(3) |
| Be(1)-N(1)#1 | 1.704(6) | N(1)-Be(1)-Cl(1) | 118.5(3) |
| Be(1)-Be(1)#1 | 2.215(10) | O(1)-Be(1)-Be(1)#1 | 114.95(18) |
| C(4)-C(5) | 1.509(6) | N(1)#1-Be(1)-Be(1)#1 | 49.7(2) |
| C(5)-C(6) | 1.501(8) | N(1)-Be(1)-Be(1)#1 | 49.4(2) |
| C(6)-C(7) | 1.459(7) | Cl(1)-Be(1)-Be(1)#1 | 141.42(14) |
| N(1)-Si(1)-C(2) | 111.93(18) | O(1)-C(4)-C(5) | 105.6(4) |
| N(1)-Si(1)-C(3) | 110.08(19) | C(6)-C(5)-C(4) | 103.7(4) |
| C(2)-Si(1)-C(3) | 108.9(2) | C(7)-C(6)-C(5) | 106.2(5) |
| N(1)-Si(1)-C(1) | 109.4(2) | C(6)-C(7)-O(1) | 106.4(4) |
| C(2)-Si(1)-C(1) | 109.0(2) | | |
| C(3)-Si(1)-C(1) | 107.4(2) | | |
| Be(1)#1-N(1)-Be(1) | 80.9(3) | | |

**Table A.23**. Anisotropic displacement parameters ($Å^2$ x $10^3$) for $C_{14}H_{36}N_2O_2Cl_2Be_2Si_2$ (**6**).

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Cl(1) | 33(1) | 48(1) | 41(1) | -5(1) | 12(1) | 0(1) |
| Si(1) | 41(1) | 31(1) | 33(1) | 0(1) | 1(1) | -1(1) |
| N(1) | 31(2) | 28(2) | 30(2) | -4(1) | 3(1) | -1(1) |
| O(1) | 39(2) | 32(1) | 36(1) | -6(1) | 3(1) | -3(1) |
| Be(1) | 30(2) | 30(2) | 32(3) | -6(2) | 6(2) | -1(2) |
| C(1) | 55(3) | 44(3) | 59(3) | 1(2) | -11(2) | 11(2) |
| C(2) | 52(3) | 39(2) | 48(3) | 5(2) | 0(2) | -3(2) |
| C(3) | 69(3) | 56(3) | 34(2) | 5(2) | 5(2) | -6(2) |
| C(4) | 67(3) | 32(2) | 40(2) | 5(2) | 8(2) | 1(2) |
| C(5) | 93(4) | 34(3) | 59(3) | -7(2) | 25(3) | -9(2) |
| C(6) | 128(6) | 52(3) | 76(4) | -27(3) | -36(4) | 13(4) |
| C(7) | 59(3) | 52(3) | 48(3) | -15(2) | -10(2) | -1(2) |

**Table A.24**. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å $^2$ x $10^3$) for $C_{14}H_{36}N_2O_2Cl_2Be_2Si_2$ (**6**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| HN1 | 13033 | 1805 | 743 | 40(12) |
| H(1A) | 13538 | -1072 | 681 | 66(9) |
| H(1B) | 13235 | -1397 | 1467 | 66(9) |
| H(1C) | 14056 | -320 | 1304 | 66(9) |
| H(2A) | 10109 | -114 | 744 | 63(9) |
| H(2B) | 10607 | -1247 | 1112 | 63(9) |
| H(2C) | 10958 | -954 | 328 | 63(9) |
| H(3A) | 12379 | 1253 | 2184 | 58(9) |
| H(3B) | 11720 | 68 | 2341 | 58(9) |
| H(3C) | 11023 | 1151 | 2043 | 58(9) |
| H(4A) | 10635 | 4829 | 196 | 54(10) |
| H(4B) | 11799 | 5076 | -218 | 54(10) |
| H(5A) | 12472 | 6301 | 611 | 130(20) |
| H(5B) | 11132 | 6466 | 772 | 130(20) |
| H(6A) | 12480 | 5698 | 1736 | 150(30) |
| H(6B) | 11183 | 5251 | 1698 | 150(30) |
| H(7A) | 11991 | 3545 | 1592 | 62(11) |
| H(7B) | 13170 | 4065 | 1331 | 62(11) |

**Table A.25**. Atomic Coordinates (x $10^4$) and Equivalent Isotropic Displacement Parameters (Å x $10^3$) for $C_{24}H_{72}N_4Sn_8Ag_4$ (**7**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Ag(1) | 2333(1) | 8695(1) | 1587(1) | 26(1) |
| Ag(2) | 2633(1) | 10457(1) | 2477(1) | 26(1) |
| Ag(3) | 2654(1) | 9076(1) | 3529(1) | 26(1) |
| Ag(4) | 2319(1) | 7321(1) | 2638(1) | 26(1) |
| Sn(1) | 2876(1) | 6141(1) | 1561(1) | 33(1) |
| Sn(2) | 913(1) | 6783(1) | 1291(1) | 33(1) |
| Sn(3) | 1627(1) | 11040(1) | 951(1) | 37(1) |
| Sn(4) | 3660(1) | 10677(1) | 1576(1) | 37(1) |
| Sn(5) | 1683(1) | 7011(1) | 3868(1) | 31(1) |
| Sn(6) | 3660(1) | 6854(1) | 4053(1) | 30(1) |
| Sn(7) | 3758(1) | 11300(1) | 3935(1) | 31(1) |
| Sn(8) | 1703(1) | 11372(1) | 3377(1) | 31(1) |
| N(1) | 2080(3) | 7144(5) | 1676(3) | 26(1) |
| N(2) | 2567(3) | 10270(5) | 1553(3) | 27(1) |
| N(3) | 2583(3) | 7485(5) | 3597(3) | 27(1) |
| N(4) | 2710(3) | 10658(5) | 3400(3) | 25(1) |
| C(1) | 2408(9) | 5391(10) | 670(5) | 69(4) |
| C(2) | 3893(5) | 7008(8) | 1640(5) | 51(2) |
| C(3) | 3148(6) | 4995(7) | 2258(5) | 51(2) |
| C(4) | 443(7) | 7037(12) | 309(5) | 68(3) |

| | | | | |
|---|---|---|---|---|
| C(5) | 316(5) | 7756(8) | 1719(5) | 47(2) |
| C(6) | 781(7) | 5199(8) | 1478(6) | 60(3) |
| C(7) | 1760(10) | 11177(11) | 70(5) | 82(5) |
| C(8) | 1544(7) | 12529(8) | 1295(6) | 68(3) |
| C(9) | 600(6) | 10191(9) | 863(5) | 54(2) |
| C(10) | 4490(6) | 9936(11) | 2366(5) | 65(3) |
| C(11) | 3874(7) | 10168(11) | 775(5) | 69(3) |
| C(12) | 3699(7) | 12332(8) | 1633(7) | 64(3) |
| C(13) | 2105(6) | 6822(10) | 4859(4) | 57(3) |
| C(14) | 783(6) | 8137(8) | 3593(6) | 58(3) |
| C(15) | 1260(6) | 5569(8) | 3453(5) | 56(3) |
| C(16) | 3555(6) | 5231(7) | 4114(4) | 49(2) |
| C(17) | 4149(6) | 7501(9) | 4963(4) | 55(3) |
| C(18) | 4378(6) | 7238(8) | 3527(5) | 51(2) |
| C(19) | 4617(5) | 10131(7) | 4102(4) | 44(2) |
| C(20) | 3661(6) | 11828(10) | 4783(5) | 60(3) |
| C(21) | 4010(6) | 12547(7) | 3435(5) | 49(2) |
| C(22) | 781(6) | 10708(9) | 2613(5) | 52(2) |
| C(23) | 1822(6) | 12983(7) | 3248(6) | 57(3) |
| C(24) | 1509(6) | 11071(9) | 4213(5) | 53(2) |

**Table A.26**. Interatomic Distances (Å) and Angles (°) for $C_{24}H_{72}N_4Sn_8Ag_4$ (**7**).

| | | | |
|---|---|---|---|
| Ag(1)-N(1) | 2.097(6) | Sn(3)-C(8) | 2.121(11) |
| Ag(1)-N(2) | 2.102(6) | Sn(3)-C(9) | 2.131(10) |
| Ag(1)-Ag(2) | 2.9967(8) | Sn(3)-C(7) | 2.143(10) |
| Ag(1)-Ag(4) | 3.0224(8) | Sn(4)-N(2) | 2.056(6) |
| Ag(2)-N(4) | 2.103(6) | Sn(4)-C(11) | 2.131(9) |
| Ag(2)-N(2 | 3.0111(8) | Sn(4)-C(10) | 2.145(12) |
| Ag(2)-Sn(4) | 3.2820(8) | Sn(4)-C(12) | 2.157(10) |
| Ag(3)-N(3) | 2.084(6) | Sn(5)-N(3) | 2.058(6) |
| Ag(3)-N(4) | 2.087(6) | Sn(5)-C(15) | 2.124(10) |
| Ag(3)-Ag(4) | 2.9880(8) | Sn(5)-C(14) | 2.128(9) |
| Ag(4)-N(3) | 2.105(6) | Sn(5)-C(13) | 2.153(9) |
| Ag(4)-N(1) | 2.118(6) | Sn(6)-N(3) | 2.050(6) |
| Ag(4)-Sn(2) | 3.3306(8) | Sn(6)-C(16) | 2.129(9) |
| Sn(1)-N(1) | 2.045(6) | Sn(6)-C(17) | 2.141(9) |
| Sn(1)-C(3) | 2.119(9) | Sn(6)-C(18) | 2.147(9) |
| Sn(1)-C(2) | 2.132(9) | Sn(7)-N(4) | 2.056(6) |
| Sn(1)-C(1) | 2.160(10) | Sn(7)-C(19) | 2.125(8) |
| Sn(2)-N(1) | 2.060(6) | Sn(7)-C(21) | 2.136(10) |
| Sn(2)-C(5) | 2.135(9) | Sn(7)-C(20) | 2.143(9) |
| Sn(2)-C(6) | 2.136(10) | Sn(8)-N(4) | 2.051(6) |
| Sn(2)-C(4) | 2.146(10) | Sn(8)-C(24) | 2.122(9) |
| Sn(3)-N(2) | 2.050(6) | Sn(8)-C(23) | 2.140(10) |

| | | | |
|---|---|---|---|
| Sn(8)-C(22) | 2.142(9) | N(3)-Ag(4)-N(1) | 178.7(2) |
| N(1)-Ag(1)-N(2) | 176.0(2) | N(3)-Ag(4)-Ag(3) | 44.22(17) |
| N(1)-Ag(1)-Ag(2) | 131.43(16) | N(1)-Ag(4)-Ag(3) | 136.10(17) |
| N(2)-Ag(1)-Ag(2) | 44.72(16) | N(3)-Ag(4)-Ag(1) | 136.19(18) |
| N(1)-Ag(1)-Ag(4) | 44.47(16) | N(1)-Ag(4)-Ag(1) | 43.91(17) |
| N(2)-Ag(1)-Ag(4) | 131.85(16) | Ag(3)-Ag(4)-Ag(1) | 92.46(2) |
| Ag(2)-Ag(1)-Ag(4) | 87.32(2) | N(3)-Ag(4)-Sn(2) | 144.61(16) |
| N(4)-Ag(2)-N(2) | 179.2(2) | N(1)-Ag(4)-Sn(2) | 36.53(16) |
| N(4)-Ag(2)-Ag(1) | 136.09(17) | Ag(3)-Ag(4)-Sn(2) | 134.78(2) |
| N(2)-Ag(2)-Ag(1) | 44.53(17) | Ag(1)-Ag(4)-Sn(2) | 66.418(19) |
| N(4)-Ag(2)-Ag(3) | 43.83(17) | N(1)-Sn(1)-C(3) | 109.6(3) |
| N(2)-Ag(2)-Ag(3) | 136.72(18) | N(1)-Sn(1)-C(2) | 107.2(3) |
| Ag(1)-Ag(2)-Ag(3) | 92.51(2) | C(3)-Sn(1)-C(2) | 110.2(4) |
| N(4)-Ag(2)-Sn(4) | 141.90(16) | N(1)-Sn(1)-C(1) | 110.7(4) |
| N(2)-Ag(2)-Sn(4) | 37.43(16) | C(3)-Sn(1)-C(1) | 108.2(5) |
| Ag(1)-Ag(2)-Sn(4) | 68.771(19) | C(2)-Sn(1)-C(1) | 111.0(5) |
| Ag(3)-Ag(2)-Sn(4) | 136.00(2) | N(1)-Sn(2)-C(5) | 107.0(3) |
| N(3)-Ag(3)-N(4) | 176.4(2) | N(1)-Sn(2)-C(6) | 108.0(4) |
| N(3)-Ag(3)-Ag(4) | 44.77(16) | C(5)-Sn(2)-C(6) | 111.4(4) |
| N(4)-Ag(3)-Ag(4) | 131.60(15) | N(1)-Sn(2)-C(4) | 112.6(4) |
| N(3)-Ag(3)-Ag(2) | 132.14(16) | C(5)-Sn(2)-C(4) | 108.6(5) |
| N(4)-Ag(3)-Ag(2) | 44.27(15) | C(6)-Sn(2)-C(4) | 109.3(5) |
| Ag(4)-Ag(3)-Ag(2) | 87.69(2) | N(1)-Sn(2)-Ag(4) | 37.75(16) |

| | | | |
|---|---|---|---|
| C(5)-Sn(2)-Ag(4) | 78.3(3) | C(15)-Sn(5)-C(13) | 108.3(5) |
| C(6)-Sn(2)-Ag(4) | 96.9(3) | C(14)-Sn(5)-C(13) | 110.0(4) |
| C(4)-Sn(2)-Ag(4) | 147.1(4) | N(3)-Sn(6)-C(16) | 109.7(3) |
| N(2)-Sn(3)-C(8) | 110.3(4) | N(3)-Sn(6)-C(17) | 109.6(4) |
| N(2)-Sn(3)-C(9) | 108.2(3) | C(16)-Sn(6)-C(17) | 110.0(4) |
| C(8)-Sn(3)-C(9) | 109.2(5) | N(3)-Sn(6)-C(18) | 106.9(3) |
| N(2)-Sn(3)-C(7) | 109.3(4) | C(16)-Sn(6)-C(18) | 110.9(4) |
| C(8)-Sn(3)-C(7) | 109.2(6) | C(17)-Sn(6)-C(18) | 109.7(4) |
| C(9)-Sn(3)-C(7) | 110.5(6) | N(4)-Sn(7)-C(19) | 107.0(3) |
| N(2)-Sn(4)-C(11) | 112.3(4) | N(4)-Sn(7)-C(21) | 108.7(3) |
| N(2)-Sn(4)-C(10) | 107.2(4) | C(19)-Sn(7)-C(21) | 110.6(4) |
| C(11)-Sn(4)-C(10) | 107.7(5) | N(4)-Sn(7)-C(20) | 108.3(3) |
| N(2)-Sn(4)-C(12) | 105.6(3) | C(19)-Sn(7)-C(20) | 111.2(4) |
| C(11)-Sn(4)-C(12) | 110.5(5) | C(21)-Sn(7)-C(20) | 110.9(5) |
| C(10)-Sn(4)-C(12) | 113.5(5) | N(4)-Sn(8)-C(24) | 109.6(3) |
| N(2)-Sn(4)-Ag(2) | 38.57(16) | N(4)-Sn(8)-C(23) | 108.2(3) |
| C(11)-Sn(4)-Ag(2) | 148.2(4) | C(24)-Sn(8)-C(23) | 111.4(5) |
| C(10)-Sn(4)-Ag(2) | 79.3(3) | N(4)-Sn(8)-C(22) | 106.1(3) |
| C(12)-Sn(4)-Ag(2) | 93.6(3) | C(24)-Sn(8)-C(22) | 109.6(4) |
| N(3)-Sn(5)-C(15) | 109.3(4) | C(23)-Sn(8)-C(22) | 111.7(4) |
| N(3)-Sn(5)-C(14) | 109.0(4) | Sn(1)-N(1)-Sn(2) | 118.7(3) |
| C(15)-Sn(5)-C(14) | 110.7(4) | Sn(1)-N(1)-Ag(1) | 114.1(3) |
| N(3)-Sn(5)-C(13) | 109.5(3) | Sn(2)-N(1)-Ag(1) | 114.1(3) |

| | | | |
|---|---|---|---|
| Sn(1)-N(1)-Ag(4) | 108.4(3) | Sn(5)-N(3)-Ag(3) | 113.6(3) |
| Sn(2)-N(1)-Ag(4) | 105.7(3) | Sn(6)-N(3)-Ag(4) | 108.5(3) |
| Ag(1)-N(1)-Ag(4) | 91.6(2) | Sn(5)-N(3)-Ag(4) | 112.5(3) |
| Sn(3)-N(2)-Sn(4) | 118.0(3) | Ag(3)-N(3)-Ag(4) | 91.0(2) |
| Sn(3)-N(2)-Ag(1) | 111.6(3) | Sn(8)-N(4)-Sn(7) | 118.2(3) |
| Sn(4)-N(2)-Ag(1) | 117.4(3) | Sn(8)-N(4)-Ag(3) | 111.1(3) |
| Sn(3)-N(2)-Ag(2) | 111.1(3) | Sn(7)-N(4)-Ag(3) | 113.5(3) |
| Sn(4)-N(2)-Ag(2) | 104.0(3) | Sn(8)-N(4)-Ag(2) | 107.2(3) |
| Ag(1)-N(2)-Ag(2) | 90.7(2) | Sn(7)-N(4)-Ag(2) | 111.7(3) |
| Sn(6)-N(3)-Sn(5) | 117.1(3) | Ag(3)-N(4)-Ag(2) | 91.9(2) |
| Sn(6)-N(3)-Ag(3) | 111.2(3) | | |

**Table A.27**. Anisotropic displacement parameters ($Å^2$ x $10^3$) for $C_{24}H_{72}N_4Sn_8Ag_4$ (**7**).

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Ag(1) | 23(1) | 26(1) | 29(1) | -2(1) | 10(1) | -3(1) |
| Ag(2) | 23(1) | 27(1) | 29(1) | -3(1) | 10(1) | -2(1) |
| Ag(3) | 23(1) | 24(1) | 29(1) | -2(1) | 9(1) | 1(1) |
| Ag(4) | 23(1) | 26(1) | 28(1) | -2(1) | 9(1) | 0(1) |
| Sn(1) | 36(1) | 32(1) | 35(1) | -6(1) | 15(1) | 4(1) |
| Sn(2) | 26(1) | 35(1) | 38(1) | -6(1) | 9(1) | -8(1) |
| Sn(3) | 41(1) | 32(1) | 36(1) | 5(1) | 11(1) | 1(1) |
| Sn(4) | 35(1) | 40(1) | 42(1) | -11(1) | 23(1) | -11(1) |
| Sn(5) | 27(1) | 29(1) | 41(1) | 3(1) | 17(1) | 3(1) |
| Sn(6) | 24(1) | 34(1) | 31(1) | 0(1) | 7(1) | 4(1) |
| Sn(7) | 26(1) | 33(1) | 33(1) | -8(1) | 7(1) | -3(1) |
| Sn(8) | 28(1) | 28(1) | 38(1) | -4(1) | 13(1) | 3(1) |
| N(1) | 23(3) | 27(3) | 29(3) | -3(2) | 9(2) | 2(2) |
| N(2) | 23(3) | 33(3) | 29(3) | 2(2) | 13(2) | -1(2) |
| N(3) | 23(3) | 32(3) | 26(3) | 0(2) | 10(2) | 3(2) |
| N(4) | 23(3) | 24(3) | 27(3) | -7(2) | 9(2) | -2(2) |
| C(1) | 103(10) | 60(7) | 45(5) | -23(5) | 27(6) | 17(6) |
| C(2) | 33(4) | 53(6) | 73(7) | 4(5) | 28(4) | 3(4) |
| C(3) | 54(6) | 31(5) | 64(6) | 11(4) | 18(4) | 11(4) |
| C(4) | 49(6) | 106(10) | 36(5) | -11(5) | -1(4) | -5(6) |
| C(5) | 39(5) | 47(5) | 62(6) | -11(4) | 24(4) | -7(4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(6) | 54(6) | 34(5) | 94(8) | -3(5) | 28(6) | -14(4) |
| C(7) | 125(12) | 89(10) | 44(6) | 28(6) | 44(7) | 41(9) |
| C(8) | 65(7) | 38(5) | 87(9) | -8(5) | 11(6) | 10(5) |
| C(9) | 42(5) | 57(6) | 50(5) | 5(4) | 0(4) | -8(4) |
| C(10) | 42(5) | 83(9) | 62(6) | 2(6) | 10(5) | -4(5) |
| C(11) | 75(8) | 87(9) | 64(7) | -31(6) | 49(6) | -9(7) |
| C(12) | 69(7) | 34(5) | 119(10) | -19(6) | 69(7) | -17(5) |
| C(13) | 59(6) | 79(8) | 37(4) | 11(5) | 24(4) | 15(5) |
| C(14) | 40(5) | 52(6) | 89(8) | 1(5) | 31(5) | 22(4) |
| C(15) | 49(6) | 42(5) | 70(7) | -12(5) | 11(5) | -5(4) |
| C(16) | 63(6) | 35(5) | 45(5) | 2(4) | 13(4) | 14(4) |
| C(17) | 48(5) | 75(7) | 33(4) | -13(4) | 3(4) | -15(5) |
| C(18) | 38(5) | 60(6) | 66(6) | 5(5) | 33(4) | -4(4) |
| C(19) | 31(4) | 40(5) | 50(5) | -6(4) | 1(3) | 9(3) |
| C(20) | 46(5) | 88(9) | 48(5) | -34(5) | 17(4) | -15(5) |
| C(21) | 39(5) | 39(5) | 66(6) | 8(4) | 16(4) | -4(4) |
| C(22) | 34(4) | 61(6) | 48(5) | -14(4) | -1(4) | 4(4) |
| C(23) | 48(5) | 30(5) | 96(8) | -1(5) | 31(5) | 5(4) |
| C(24) | 53(6) | 69(7) | 44(5) | 1(5) | 25(4) | 5(5) |

**Table A.28**. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å $^2$ x $10^3$) for $C_{24}H_{72}N_4Sn_8Ag_4$ (**7**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 2072 | 4848 | 690 | 90(30) |
| H(1B) | 2824 | 5120 | 563 | 90(30) |
| H(1C) | 2123 | 5874 | 365 | 90(30) |
| H(2A) | 3745 | 7624 | 1406 | 56(18) |
| H(2B) | 4220 | 6614 | 1485 | 56(18) |
| H(2C) | 4168 | 7172 | 2062 | 56(18) |
| H(3A) | 3372 | 5308 | 2653 | 70(20) |
| H(3B) | 3509 | 4522 | 2198 | 70(20) |
| H(3C) | 2686 | 4642 | 2234 | 70(20) |
| H(4A) | 673 | 7635 | 211 | 90(30) |
| H(4B) | -106 | 7128 | 179 | 90(30) |
| H(4C) | 554 | 6460 | 102 | 90(30) |
| H(5A) | 149 | 7363 | 1995 | 70(20) |
| H(5B) | -125 | 8054 | 1410 | 70(20) |
| H(5C) | 658 | 8285 | 1943 | 70(20) |
| H(6A) | 902 | 4784 | 1186 | 120(40) |
| H(6B) | 258 | 5074 | 1445 | 120(40) |
| H(6C) | 1124 | 5035 | 1884 | 120(40) |
| H(7A) | 2209 | 11579 | 113 | 180(60) |
| H(7B) | 1312 | 11499 | -217 | 180(60) |
| H(7C) | 1819 | 10512 | -79 | 180(60) |

| | | | | |
|---|---|---|---|---|
| H(8A) | 1594 | 12482 | 1718 | 120(40) |
| H(8B) | 1052 | 12822 | 1062 | 120(40) |
| H(8C) | 1949 | 12952 | 1261 | 120(40) |
| H(9A) | 564 | 9609 | 606 | 110(30) |
| H(9B) | 155 | 10616 | 684 | 110(30) |
| H(9C) | 623 | 9969 | 1261 | 110(30) |
| H(10A) | 4313 | 9263 | 2406 | 170(50) |
| H(10B) | 4546 | 10321 | 2729 | 170(50) |
| H(10C) | 4980 | 9895 | 2314 | 170(50) |
| H(11A) | 4130 | 9521 | 857 | 240(80) |
| H(11B) | 4195 | 10654 | 673 | 240(80) |
| H(11C) | 3393 | 10103 | 438 | 240(80) |
| H(12A) | 3458 | 12615 | 1230 | 130(40) |
| H(12B) | 4226 | 12553 | 1801 | 130(40) |
| H(12C) | 3429 | 12558 | 1892 | 130(40) |
| H(13A) | 2536 | 6362 | 4981 | 100(30) |
| H(13B) | 1700 | 6552 | 4980 | 100(30) |
| H(13C) | 2266 | 7470 | 5053 | 100(30) |
| H(14A) | 999 | 8794 | 3734 | 150(50) |
| H(14B) | 401 | 7976 | 3768 | 150(50) |
| H(14C) | 548 | 8143 | 3154 | 150(50) |
| H(15A) | 1251 | 5564 | 3039 | 85 |
| H(15B) | 747 | 5462 | 3451 | 85 |

| | | | | |
|---|---|---|---|---|
| H(15C) | 1593 | 5037 | 3682 | 85 |
| H(16A) | 3120 | 5077 | 4231 | 70(20) |
| H(16B) | 4016 | 4964 | 4415 | 70(20) |
| H(16C) | 3480 | 4929 | 3723 | 70(20) |
| H(17A) | 4552 | 7969 | 4976 | 90(30) |
| H(17B) | 4357 | 6967 | 5256 | 90(30) |
| H(17C) | 3754 | 7854 | 5059 | 90(30) |
| H(18A) | 4207 | 6863 | 3149 | 100(30) |
| H(18B) | 4905 | 7066 | 3759 | 100(30) |
| H(18C) | 4340 | 7953 | 3440 | 100(30) |
| H(19A) | 4608 | 9710 | 4435 | 90(30) |
| H(19B) | 5117 | 10437 | 4205 | 90(30) |
| H(19C) | 4510 | 9723 | 3740 | 90(30) |
| H(20A) | 3261 | 12332 | 4694 | 60(20) |
| H(20B) | 4142 | 12121 | 5038 | 60(20) |
| H(20C) | 3536 | 11266 | 4992 | 60(20) |
| H(21A) | 4149 | 12284 | 3104 | 110(30) |
| H(21B) | 4431 | 12938 | 3705 | 110(30) |
| H(21C) | 3562 | 12972 | 3271 | 110(30) |
| H(22A) | 853 | 9985 | 2611 | 210(70) |
| H(22B) | 787 | 10992 | 2236 | 210(70) |
| H(22C) | 294 | 10851 | 2654 | 210(70) |
| H(23A) | 2100 | 13294 | 3637 | 140(40) |

| | | | | |
|---|---|---|---|---|
| H(23B) | 1319 | 13286 | 3075 | 140(40) |
| H(23C) | 2100 | 13084 | 2976 | 140(40) |
| H(24A) | 1491 | 10350 | 4269 | 130(40) |
| H(24B) | 1028 | 11370 | 4192 | 130(40) |
| H(24C) | 1921 | 11359 | 4551 | 130(40) |

**Table A.29**. Atomic Coordinates (x $10^4$) and Equivalent Isotropic Displacement Parameters (Å x $10^3$) for $C_{24}H_{72}N_4Si_4Sn_4Ag_4$ (**8**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Ag(1) | 4236(1) | 1062(1) | 8759(1) | 33(1) |
| Sn(1) | 4659(1) | 2812(1) | 11330(1) | 49(1) |
| Si(1) | 4659(1) | 2812(1) | 11330(1) | 49(1) |
| Sn(2) | 3286(1) | 0 | 5356(1) | 46(1) |
| Si(2) | 3286(1) | 0 | 5356(1) | 46(1) |
| Sn(3) | 2658(1) | 0 | 8123(1) | 48(1) |
| Si(3) | 2658(1) | 0 | 8123(1) | 48(1) |
| N(1) | 5000 | 2134(5) | 10000 | 34(2) |
| N(2) | 3474(4) | 0 | 7534(10) | 36(2) |
| C(1) | 5324(18) | 3760(20) | 12470(40) | 105(8) |
| C(1A) | 5557(11) | 3253(15) | 13240(20) | 69(5) |
| C(2) | 3648(14) | 3300(19) | 9850(30) | 89(7) |
| C(2A) | 4035(12) | 3874(14) | 10190(30) | 68(5) |
| C(3) | 4590(15) | 1880(17) | 12740(30) | 82(6) |
| C(3A) | 4151(12) | 1892(16) | 12060(30) | 72(5) |
| C(4) | 4250(20) | 80(130) | 5320(40) | 69(17) |
| C(4A) | 4150(20) | -380(30) | 5280(40) | 40(9) |
| C(5) | 3039(13) | 1456(16) | 4590(30) | 77(6) |
| C(5A) | 2612(14) | 962(17) | 4170(30) | 86(7) |
| C(6) | 2308(13) | 1416(17) | 7740(30) | 83(6) |

| | | | | |
|---|---|---|---|---|
| C(6A) | 1907(17) | 840(20) | 6710(30) | 109(9) |
| C(7) | 3040(20) | 270(30) | 10150(50) | 55(12) |
| C(7A) | 3000(20) | -330(30) | 10560(50) | 58(12) |

**Table A.30**. Interatomic Distances (Å) and Angles (°) for $C_{24}H_{72}N_4Si_4Sn_4Ag_4$ (**8**).

| | | | |
|---|---|---|---|
| Ag(1)-N(2) | 2.118(5) | Sn(2)-Ag(1)#1 | 3.3281(12) |
| Ag(1)-N(1) | 2.132(5) | Sn(3)-C(7)# | 1.78(4) |
| Ag(1)-Ag(1)#1 | 2.9949(11) | Sn(3)-C(7) | 1.78(4) |
| Ag(1)-Ag(1)#2 | 3.0104(11) | Sn(3)-C(6A)#1 | 1.95(3) |
| Ag(1)-Sn(1) | 3.3151(11) | Sn(3)-C(6A) | 1.95(3) |
| Ag(1)-Sn(2) | 3.3281(12) | Sn(3)-N(2) | 2.000(8) |
| Sn(1)-C(1) | 1.88(3) | Sn(3)-C(6) | 2.10(2) |
| Sn(1)-C(3) | 1.93(2) | Sn(3)-C(6)#1 | 2.10(2) |
| Sn(1)-N(1) | 1.952(4) | Sn(3)-C(7A)#1 | 2.16(5) |
| Sn(1)-C(2A) | 1.97(2) | Sn(3)-C(7A) | 2.16(5) |
| Sn(1)-C(3A | 2.05(2) | N(1)-Si(1)#2 | 1.952(4) |
| Sn(1)-C(2) | 2.07(3) | N(1)-Sn(1)#2 | 1.952(4) |
| Sn(2)-C(4A)#1 | 1.91(4) | N(1)-Ag(1)#2 | 2.132(5) |
| Sn(2)-C(4A) | 1.91(4) | N(2)-Ag(1)#1 | 2.118(5) |
| Sn(2)-C(5A)#1 | 1.92(2) | C(1)-C(1A) | 0.98(3) |
| Sn(2)-C(5A) | 1.92(2) | C(2)-C(2A) | 1.08(3) |
| Sn(2)-N(2) | 1.940(9) | C(3)-C(3A) | 0.86(3) |
| Sn(2)-C(4)#1 | 2.03(4) | C(4)-C(4)#1 | 0.2(4) |
| Sn(2)-C(4) | 2.03(4) | C(4)-C(4A)#1 | 0.47(17) |
| Sn(2)-C(5)#1 | 2.16(2) | C(4)-C(4A) | 0.69(17) |
| Sn(2)-C(5) | 2.16(2) | C(4A)-C(4)#1 | 0.47(17) |

| | | | |
|---|---|---|---|
| C(4A)-C(4A)#1 | 1.08(8) | C(1)-Sn(1)-C(3) | 109.7(13) |
| C(5)-C(5A) | 1.06(3) | C(1)-Sn(1)-N(1) | 109.9(10) |
| C(6)-C(6A) | 1.27(3) | C(3)-Sn(1)-N(1) | 106.2(7) |
| C(7)-C(7A)#1 | 0.43(6) | C(1)-Sn(1)-C(2A) | 85.3(12) |
| C(7)-C(7)#1 | 0.75(7) | C(3)-Sn(1)-C(2A) | 132.3(10) |
| C(7)-C(7A) | 0.94(4) | N(1)-Sn(1)-C(2A) | 110.5(7) |
| C(7A)-C(7)#1 | 0.43(6) | C(1)-Sn(1)-C(3A) | 129.0(12) |
| C(7A)-C(7A)#1 | 0.93(8) | C(3)-Sn(1)-C(3A) | 25.3(8) |
| N(2)-Ag(1)-N(1) | 179.7(2) | N(1)-Sn(1)-C(3A) | 107.9(7) |
| N(2)-Ag(1)-Ag(1)#1 | 45.00(14) | C(2A)-Sn(1)-C(3A) | 111.8(10) |
| N(1)-Ag(1)-Ag(1)#1 | 135.09(14) | C(1)-Sn(1)-C(1A) | 28.6(10) |
| N(2)-Ag(1)-Ag(1)#2 | 135.00(14) | C(3)-Sn(1)-C(1A) | 84.3(10) |
| N(1)-Ag(1)-Ag(1)#2 | 45.09(14) | N(1)-Sn(1)-C(1A) | 106.4(6) |
| Ag(1)#1-Ag(1)-Ag(1)#2 | 90.0 | C(2A)-Sn(1)-C(1A) | 112.5(9) |
| N(2)-Ag(1)-Sn(1) | 145.8(2) | C(3A)-Sn(1)-C(1A) | 107.5(9) |
| N(1)-Ag(1)-Sn(1) | 33.95(6) | C(1)-Sn(1)-C(2) | 115.2(12) |
| Ag(1)#1-Ag(1)-Sn(1) | 138.052(19) | C(3)-Sn(1)-C(2) | 110.0(11) |
| Ag(1)#2-Ag(1)-Sn(1) | 64.60(2) | N(1)-Sn(1)-C(2) | 105.3(7) |
| N(2)-Ag(1)-Sn(2) | 33.2(2) | C(2A)-Sn(1)-C(2) | 31.0(8) |
| N(1)-Ag(1)-Sn(2) | 147.03(6) | C(3A)-Sn(1)-C(2) | 85.6(10) |
| Ag(1)#1-Ag(1)-Sn(2) | 63.260(14) | C(1A)-Sn(1)-C(2) | 139.6(10) |
| Ag(1)#2-Ag(1)-Sn(2) | 137.48(3) | C(1)-Sn(1)-Ag(1) | 147.5(10) |
| Sn(1)-Ag(1)-Sn(2) | 155.41(2) | C(3)-Sn(1)-Ag(1) | 86.3(7) |

| | | | |
|---|---|---|---|
| N(1)-Sn(1)-Ag(1) | 37.59(12) | C(5A)-Sn(2)-C(4) | 115(4) |
| C(2A)-Sn(1)-Ag(1) | 105.0(6) | N(2)-Sn(2)-C(4) | 106.5(11) |
| C(3A)-Sn(1)-Ag(1) | 76.3(6) | C(4)#1-Sn(2)-C(4) | 7(10) |
| C(1A)-Sn(1)-Ag(1) | 136.6(6) | C(4A)#1-Sn(2)-C(5)#1 | 110.1(13) |
| C(2)-Sn(1)-Ag(1) | 83.1(7) | C(4A)-Sn(2)-C(5)#1 | 78.8(13) |
| C(4A)#1-Sn(2)-C(4A) | 33(2) | C(5A)#1-Sn(2)-C(5)#1 | 29.2(8) |
| C(4A)#1-Sn(2)-C(5A)#1 | 129.1(13) | C(5A)-Sn(2)-C(5)#1 | 117.8(11) |
| C(4A)-Sn(2)-C(5A)#1 | 103.3(13) | N(2)-Sn(2)-C(5)#1 | 105.6(6) |
| C(4A)#1-Sn(2)-C(5A) | 103.3(13) | C(4)#1-Sn(2)-C(5)#1 | 92(5) |
| C(4A)-Sn(2)-C(5A) | 129.1(13) | C(4)-Sn(2)-C(5)#1 | 98(5) |
| C(5A)#1-Sn(2)-C(5A) | 89.9(16) | C(4A)#1-Sn(2)-C(5) | 78.8(13) |
| C(4A)#1-Sn(2)-N(2) | 106.8(11) | C(4A)-Sn(2)-C(5) | 110.1(13) |
| C(4A)-Sn(2)-N(2) | 106.8(11) | C(5A)#1-Sn(2)-C(5) | 117.8(11) |
| C(5A)#1-Sn(2)-N(2) | 112.8(8) | C(5A)-Sn(2)-C(5) | 29.2(8) |
| C(5A)-Sn(2)-N(2) | 112.8(8) | N(2)-Sn(2)-C(5) | 105.6(6) |
| C(4A)#1-Sn(2)-C(4)#1 | 20(5) | C(4)#1-Sn(2)-C(5) | 98(5) |
| C(4A)-Sn(2)-C(4)#1 | 13(6) | C(4)-Sn(2)-C(5) | 92(5) |
| C(5A)#1-Sn(2)-C(4)#1 | 115(4) | C(5)#1-Sn(2)-C(5) | 143.1(12) |
| C(5A)-Sn(2)-C(4)#1 | 120(4) | C(4A)#1-Sn(2)-Ag(1) | 75.2(11) |
| N(2)-Sn(2)-C(4)#1 | 106.5(11) | C(4A)-Sn(2)-Ag(1) | 90.0(10) |
| C(4A)#1-Sn(2)-C(4) | 13(6) | C(5A)#1-Sn(2)-Ag(1) | 149.4(8) |
| C(4A)-Sn(2)-C(4) | 20(5) | C(5A)-Sn(2)-Ag(1) | 103.0(8) |
| C(5A)#1-Sn(2)-C(4) | 120(4) | N(2)-Sn(2)-Ag(1) | 36.69(15) |

| | | | |
|---|---|---|---|
| C(4)#1-Sn(2)-Ag(1) | 83(3) | C(6A)-Sn(3)-N(2) | 108.7(10) |
| C(4)-Sn(2)-Ag(1) | 80(3) | C(7)#1-Sn(3)-C(6) | 110.0(14) |
| C(5)#1-Sn(2)-Ag(1) | 135.1(6) | C(7)-Sn(3)-C(6) | 86.7(14) |
| C(5)-Sn(2)-Ag(1) | 81.6(6) | C(6A)#1-Sn(3)-C(6) | 110.1(12) |
| C(4A)#1-Sn(2)-Ag(1)#1 | 90.0(10) | C(6A)-Sn(3)-C(6) | 36.3(10) |
| C(4A)-Sn(2)-Ag(1)#1 | 75.2(11) | N(2)-Sn(3)-C(6) | 102.8(6) |
| C(5A)#1-Sn(2)-Ag(1)#1 | 103.0(8) | C(7)#1-Sn(3)-C(6)#1 | 86.7(14) |
| C(5A)-Sn(2)-Ag(1)#1 | 149.4(8) | C(7)-Sn(3)-C(6)#1 | 110.0(14) |
| N(2)-Sn(2)-Ag(1)#1 | 36.69(15) | C(6A)#1-Sn(3)-C(6)#1 | 36.3(10) |
| C(4)#1-Sn(2)-Ag(1)#1 | 80(3) | C(6A)-Sn(3)-C(6)#1 | 110.1(12) |
| C(4)-Sn(2)-Ag(1)#1 | 83(3) | N(2)-Sn(3)-C(6)#1 | 102.8(6) |
| C(5)#1-Sn(2)-Ag(1)#1 | 81.6(6) | C(6)-Sn(3)-C(6)#1 | 143.7(13) |
| C(5)-Sn(2)-Ag(1)#1 | 135.1(6) | C(7)#1-Sn(3)-C(7A)#1 | 25.3(11) |
| Ag(1)-Sn(2)-Ag(1)#1 | 53.48(3) | C(7)-Sn(3)-C(7A)#1 | 6(2) |
| C(7)#1-Sn(3)-C(7) | 24(2) | C(6A)#1-Sn(3)-C(7A)#1 | 131.5(15) |
| C(7)#1-Sn(3)-C(6A)#1 | 117.6(15) | C(6A)-Sn(3)-C(7A)#1 | 113.8(15) |
| C(7)-Sn(3)-C(6A)#1 | 135.9(16) | N(2)-Sn(3)-C(7A)#1 | 112.4(12) |
| C(7)#1-Sn(3)-C(6A) | 135.9(16) | C(6)-Sn(3)-C(7A)#1 | 84.7(13) |
| C(7)-Sn(3)-C(6A) | 117.6(15) | C(6)#1-Sn(3)-C(7A)#1 | 108.4(13) |
| C(6A)#1-Sn(3)-C(6A) | 74.5(18) | C(7)#1-Sn(3)-C(7A) | 6(2) |
| C(7)#1-Sn(3)-N(2) | 106.5(13) | C(7)-Sn(3)-C(7A) | 25.3(11) |
| C(7)-Sn(3)-N(2) | 106.5(13) | C(6A)#1-Sn(3)-C(7A) | 113.8(15) |
| C(6A)#1-Sn(3)-N(2) | 108.7(10) | C(6A)-Sn(3)-C(7A) | 131.5(15) |

| | | | |
|---|---|---|---|
| N(2)-Sn(3)-C(7A) | 112.4(12) | C(2)-C(2A)-Sn(1) | 79.5(17) |
| C(6)-Sn(3)-C(7A) | 108.4(13) | C(3A)-C(3)-Sn(1) | 80(2) |
| C(6)#1-Sn(3)-C(7A) | 84.7(13) | C(3)-C(3A)-Sn(1) | 74(2) |
| C(7A)#1-Sn(3)-C(7A) | 25(2) | C(4)#1-C(4)-C(4A)#1 | 155(10) |
| Si(1)#2-N(1)-Sn(1)#2 | 0.00(4) | C(4)#1-C(4)-C(4A) | 17(5) |
| Si(1)#2-N(1)-Sn(1) | 121.4(4) | C(4A)#1-C(4)-C(4A) | 138(10) |
| Sn(1)#2-N(1)-Sn(1) | 121.4(4) | C(4)#1-C(4)-Sn(2) | 87(5) |
| Si(1)#2-N(1)-Ag(1) | 112.14(8) | C(4A)#1-C(4)-Sn(2) | 69(10) |
| Sn(1)#2-N(1)-Ag(1) | 112.14(8) | C(4A)-C(4)-Sn(2) | 70(7) |
| Sn(1)-N(1)-Ag(1) | 108.46(8) | C(4)#1-C(4A)-C(4) | 8(10) |
| Si(1)#2-N(1)-Ag(1)#2 | 108.46(8) | C(4)#1-C(4A)-C(4A)#1 | 25(10) |
| Sn(1)#2-N(1)-Ag(1)#2 | 108.46(8) | C(4)-C(4A)-C(4A)#1 | 17(5) |
| Sn(1)-N(1)-Ag(1)#2 | 112.14(8) | C(4)#1-C(4A)-Sn(2) | 98(10) |
| Ag(1)-N(1)-Ag(1)#2 | 89.8(3) | C(4)-C(4A)-Sn(2) | 90(6) |
| Sn(2)-N(2)-Sn(3) | 120.2(4) | C(4A)#1-C(4A)-Sn(2) | 73.5(11) |
| Sn(2)-N(2)-Ag(1) | 110.1(3) | C(5A)-C(5)-Sn(2) | 62.6(18) |
| Sn(3)-N(2)-Ag(1) | 111.2(3) | C(5)-C(5A)-Sn(2) | 88(2) |
| Sn(2)-N(2)-Ag(1)#1 | 110.1(3) | C(6A)-C(6)-Sn(3) | 65.3(17) |
| Sn(3)-N(2)-Ag(1)#1 | 111.2(3) | C(6)-C(6A)-Sn(3) | 78.3(19) |
| Ag(1)-N(2)-Ag(1)#1 | 90.0(3) | C(7A)#1-C(7)-C(7)#1 | 102(9) |
| C(1A)-C(1)-Sn(1) | 85(2) | C(7A)#1-C(7)-C(7A) | 75(10) |
| C(1)-C(1A)-Sn(1) | 6(2) | C(7)#1-C(7)-C(7A) | 27(3) |
| C(2A)-C(2)-Sn(1) | 69.4(17) | C(7A)#1-C(7)-Sn(3) | 149(10) |

| | | | |
|---|---|---|---|
| C(7)#1-C(7)-Sn(3) | 77.8(12) | C(7)#1-C(7A)-Sn(3) | 25(9) |
| C(7A)-C(7)-Sn(3) | 101(4) | C(7A)#1-C(7A)-Sn(3) | 77.6(11) |
| C(7)#1-C(7A)-C(7A)#1 | 78(9) | C(7)-C(7A)-Sn(3) | 54(3) |
| C(7)#1-C(7A)-C(7) | 51(9) | | |
| C(7A)#1-C(7A)-C(7) | 27(3) | | |

**Table A.31**. Anisotropic displacement parameters ($Å^2$ x $10^3$) for $C_{24}H_{72}N_4Si_4Sn_4Ag_4$ (**8**).

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Ag(1) | 32(1) | 30(1) | 38(1) | 0(1) | 16(1) | 0(1) |
| Sn(1) | 57(1) | 38(1) | 50(1) | -1(1) | 22(1) | 5(1) |
| Si(1) | 57(1) | 38(1) | 50(1) | -1(1) | 22(1) | 5(1) |
| Sn(2) | 37(1) | 64(1) | 35(1) | 0 | 14(1) | 0 |
| Si(2) | 37(1) | 64(1) | 35(1) | 0 | 14(1) | 0 |
| Sn(3) | 25(1) | 77(1) | 41(1) | 0 | 14(1) | 0 |
| Si(3) | 25(1) | 77(1) | 41(1) | 0 | 14(1) | 0 |
| N(1) | 26(4) | 31(4) | 37(4) | 0 | 7(3) | 0 |
| N(2) | 24(4) | 36(4) | 43(4) | 0 | 11(3) | 0 |

**Table A.32**. Atomic Coordinates (x $10^4$) and Equivalent Isotropic Displacement Parameters (Å x $10^3$) for $C_{24}H_{72}N_4Ge_4Sn_4Ag_4$ (**9**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Ag(1) | 763(1) | 1057(1) | 6255(1) | 26(1) |
| Sn(1) | 338(1) | 2808(1) | 3704(1) | 40(1) |
| Ge(1) | 338(1) | 2808(1) | 3704(1) | 40(1) |
| Sn(2) | 2346(1) | 0 | 6954(1) | 48(1) |
| Ge(2) | 2346(1) | 0 | 6954(1) | 48(1) |
| Sn(3) | 1712(1) | 0 | 9614(1) | 44(1) |
| Ge(3) | 1712(1) | 0 | 9614(1) | 44(1) |
| N(1) | 0 | 2092(5) | 5000 | 29(2) |
| N(2) | 1521(4) | 0 | 7479(9) | 27(2) |
| C(1) | 996(14) | 3853(16) | 4880(30) | 69(6) |
| C(1A) | 1397(12) | 3331(16) | 5260(20) | 64(5) |
| C(2) | -275(15) | 3898(17) | 2630(30) | 80(7) |
| C(2A) | -577(11) | 3274(15) | 1780(20) | 57(5) |
| C(3) | 843(11) | 1864(14) | 2870(20) | 52(4) |
| C(3A) | 420(12) | 1966(14) | 2150(30) | 58(5) |
| C(4) | 2691(14) | 1525(18) | 7270(30) | 77(7) |
| C(4A) | 3138(16) | 818(19) | 8340(30) | 87(8) |
| C(5) | 2031(19) | 0 | 4650(40) | 67(9) |
| C(5A) | 1988(14) | -440(18) | 4650(30) | 14(4) |
| C(6) | 730(30) | 190(40) | 9610(50) | 50(17) |

| | | | | |
|---|---|---|---|---|
| C(6A) | 880(20) | -270(30) | 9870(50) | 32(11) |
| C(7) | 2412(16) | 940(20) | 10800(30) | 87(8) |
| C(7A) | 2039(13) | 1394(17) | 10450(30) | 65(6) |

**Table A.33**. Interatomic Distances (Å) and Angles (°) for $C_{24}H_{72}N_4Ge_4Sn_4Ag_4$ (**9**).

| | | | |
|---|---|---|---|
| Ag(1)-N(1) | 2.107(5) | Sn(3)-C(6A)#1 | 1.90(4) |
| Ag(1)-N(2) | 2.118(5) | Sn(3)-N(2) | 1.912(8) |
| Ag(1)-Ag(1)#1 | 2.9992(11) | Sn(3)-C(7) | 1.93(3) |
| Ag(1)-Ag(1)#2 | 3.0233(10) | Sn(3)-C(7)#1 | 1.93(3) |
| Ag(1)-Sn(3) | 3.3122(11) | Sn(3)-C(6) | 2.06(5) |
| Ag(1)-Sn(1) | 3.3265(9) | Sn(3)-C(6)#1 | 2.06(5) |
| Sn(1)-N(1) | 1.961(4) | Sn(3)-C(7A)#1 | 2.13(2) |
| Sn(1)-C(3A) | 1.98(2) | Sn(3)-C(7A) | 2.13(2) |
| Sn(1)-C(2) | 1.98(3) | Sn(3)-Ag(1)#1 | 3.3122(11) |
| Sn(1)-C(1) | 2.00(2) | N(1)-Ge(1)#2 | 1.961(4) |
| Sn(1)-C(3) | 2.07(2) | N(1)-Sn(1)#2 | 1.961(4) |
| Sn(1)-C(2A) | 2.09(2) | N(1)-Ag(1)#2 | 2.107(5) |
| Sn(1)-C(1A) | 2.18(2) | N(2)-Ag(1)#1 | 2.118(5) |
| Sn(2)-C(4A) | 1.98(3) | C(1)-C(1A) | 1.05(3) |
| Sn(2)-C(4A)#1 | 1.98(3) | C(2)-C(2A) | 1.18(3) |
| Sn(2)-N(2) | 1.986(8) | C(3)-C(3A) | 0.86(2) |
| Sn(2)-C(5) | 2.02(4) | C(4)-C(4A) | 1.44(4) |
| Sn(2)-C(5A) | 2.09(2) | C(5)-C(5A) | 0.63(3) |
| Sn(2)-C(5A)#1 | 2.09(2) | C(5)-C(5A)#1 | 0.63(3) |
| Sn(2)-C(4) | 2.26(3) | C(5A)-C(5A)#1 | 1.25(5) |
| Sn(2)-C(4)#1 | 2.26(3) | C(6)-C(6A)#1 | 0.32(7) |
| Sn(3)-C(6A) | 1.90(4) | C(6)-C(6)#1 | 0.55(12) |

| | | | |
|---|---|---|---|
| C(6)-C(6A) | 0.72(5) | C(3A)-Sn(1)-C(1) | 127.7(10) |
| C(6A)-C(6)#1 | 0.32(7) | C(2)-Sn(1)-C(1) | 80.7(11) |
| C(6A)-C(6A)#1 | 0.76(8) | N(1)-Sn(1)-C(3) | 107.2(6) |
| C(7)-C(7A) | 0.95(3) | C(3A)-Sn(1)-C(3) | 24.4(7) |
| N(1)-Ag(1)-N(2) | 178.9(2) | C(2)-Sn(1)-C(3) | 128.4(10) |
| N(1)-Ag(1)-Ag(1)#1 | 134.16(14) | C(1)-Sn(1)-C(3) | 111.3(10) |
| N(2)-Ag(1)-Ag(1)#1 | 44.91(15) | N(1)-Sn(1)-C(2A) | 106.8(6) |
| N(1)-Ag(1)-Ag(1)#2 | 44.16(14) | C(3A)-Sn(1)-C(2A) | 82.4(9) |
| N(2)-Ag(1)-Ag(1)#2 | 134.91(15) | C(2)-Sn(1)-C(2A) | 33.5(9) |
| Ag(1)#1-Ag(1)-Ag(1)#2 | 90.0 | C(1)-Sn(1)-C(2A) | 113.3(9) |
| N(1)-Ag(1)-Sn(3) | 148.15(6) | C(3)-Sn(1)-C(2A) | 106.2(8) |
| N(2)-Ag(1)-Sn(3) | 32.8(2) | N(1)-Sn(1)-C(1A) | 105.9(6) |
| Ag(1)#1-Ag(1)-Sn(3) | 63.079(12) | C(3A)-Sn(1)-C(1A) | 109.3(9) |
| Ag(1)#2-Ag(1)-Sn(3) | 138.11(3) | C(2)-Sn(1)-C(1A) | 108.4(10) |
| N(1)-Ag(1)-Sn(1) | 33.71(6) | C(1)-Sn(1)-C(1A) | 28.8(8) |
| N(2)-Ag(1)-Sn(1) | 146.1(2) | C(3)-Sn(1)-C(1A) | 87.5(8) |
| Ag(1)#1-Ag(1)-Sn(1) | 138.301(16) | C(2A)-Sn(1)-C(1A) | 138.7(9) |
| Ag(1)#2-Ag(1)-Sn(1) | 64.251(18) | N(1)-Sn(1)-Ag(1) | 36.62(12) |
| Sn(3)-Ag(1)-Sn(1) | 155.33(2) | C(3A)-Sn(1)-Ag(1) | 91.4(6) |
| N(1)-Sn(1)-C(3A) | 110.0(6) | C(2)-Sn(1)-Ag(1) | 150.5(8) |
| N(1)-Sn(1)-C(2) | 114.3(8) | C(1)-Sn(1)-Ag(1) | 104.0(7) |
| C(3A)-Sn(1)-C(2) | 108.9(10) | C(3)-Sn(1)-Ag(1) | 77.7(5) |
| N(1)-Sn(1)-C(1) | 111.8(7) | C(2A)-Sn(1)-Ag(1) | 137.1(6) |

| | | | |
|---|---|---|---|
| C(1A)-Sn(1)-Ag(1) | 83.4(6) | C(4A)#1-Sn(2)-C(4)#1 | 39.2(10) |
| C(4A)-Sn(2)-C(4A)#1 | 71.9(16) | N(2)-Sn(2)-C(4)#1 | 102.9(6) |
| C(4A)-Sn(2)-N(2) | 112.5(9) | C(5)-Sn(2)-C(4)#1 | 94.6(7) |
| C(4A)#1-Sn(2)-N(2) | 112.5(9) | C(5A)-Sn(2)-C(4)#1 | 78.6(9) |
| C(4A)-Sn(2)-C(5) | 120.9(11) | C(5A)#1-Sn(2)-C(4)#1 | 111.9(9) |
| C(4A)#1-Sn(2)-C(5) | 120.9(11) | C(4)-Sn(2)-C(4)#1 | 146.8(13) |
| N(2)-Sn(2)-C(5) | 112.4(11) | C(6A)-Sn(3)-C(6A)#1 | 23(3) |
| C(4A)-Sn(2)-C(5A) | 133.8(11) | C(6A)-Sn(3)-N(2) | 111.7(14) |
| C(4A)#1-Sn(2)-C(5A) | 110.0(11) | C(6A)#1-Sn(3)-N(2) | 111.7(14) |
| N(2)-Sn(2)-C(5A) | 108.9(7) | C(6A)-Sn(3)-C(7) | 123.8(16) |
| C(5)-Sn(2)-C(5A) | 17.5(7) | C(6A)#1-Sn(3)-C(7) | 106.4(16) |
| C(4A)-Sn(2)-C(5A)#1 | 110.0(11) | N(2)-Sn(3)-C(7) | 112.3(9) |
| C(4A)#1-Sn(2)-C(5A)#1 | 133.8(11) | C(6A)-Sn(3)-C(7)#1 | 106.4(15) |
| N(2)-Sn(2)-C(5A)#1 | 108.9(7) | C(6A)#1-Sn(3)-C(7)#1 | 123.8(16) |
| C(5)-Sn(2)-C(5A)#1 | 17.5(7) | N(2)-Sn(3)-C(7)#1 | 112.3(8) |
| C(5A)-Sn(2)-C(5A)#1 | 34.7(14) | C(7)-Sn(3)-C(7)#1 | 87.1(18) |
| C(4A)-Sn(2)-C(4) | 39.2(10) | C(6A)-Sn(3)-C(6) | 20.4(15) |
| C(4A)#1-Sn(2)-C(4) | 110.5(11) | C(6A)#1-Sn(3)-C(6) | 8(2) |
| N(2)-Sn(2)-C(4) | 102.9(6) | N(2)-Sn(3)-C(6) | 105.0(14) |
| C(5)-Sn(2)-C(4) | 94.6(7) | C(7)-Sn(3)-C(6) | 113.5(17) |
| C(5A)-Sn(2)-C(4) | 111.9(9) | C(7)#1-Sn(3)-C(6) | 125.7(19) |
| C(5A)#1-Sn(2)-C(4) | 78.6(9) | C(6A)-Sn(3)-C(6)#1 | 8(2) |
| C(4A)-Sn(2)-C(4)#1 | 110.5(11) | C(6A)#1-Sn(3)-C(6)#1 | 20.4(15) |

| | | | |
|---|---|---|---|
| N(2)-Sn(3)-C(6)#1 | 105.0(14) | C(7)#1-Sn(3)-Ag(1)#1 | 103.6(9) |
| C(7)-Sn(3)-C(6)#1 | 125.7(19) | C(6)-Sn(3)-Ag(1)#1 | 83.9(13) |
| C(7)#1-Sn(3)-C(6)#1 | 113.5(17) | C(6)#1-Sn(3)-Ag(1)#1 | 76.8(15) |
| C(6)-Sn(3)-C(6)#1 | 15(3) | C(7A)#1-Sn(3)-Ag(1)#1 | 84.3(6) |
| C(6A)-Sn(3)-C(7A)#1 | 85.6(14) | C(7A)-Sn(3)-Ag(1)#1 | 137.9(6) |
| C(6A)#1-Sn(3)-C(7A)#1 | 107.1(14) | C(6A)-Sn(3)-Ag(1) | 91.8(13) |
| N(2)-Sn(3)-C(7A)#1 | 106.6(6) | C(6A)#1-Sn(3)-Ag(1) | 81.4(13) |
| C(7)-Sn(3)-C(7A)#1 | 112.6(13) | N(2)-Sn(3)-Ag(1) | 36.80(15) |
| C(7)#1-Sn(3)-C(7A)#1 | 26.5(9) | C(7)-Sn(3)-Ag(1) | 103.6(9) |
| C(6)-Sn(3)-C(7A)#1 | 106.1(18) | C(7)#1-Sn(3)-Ag(1) | 149.1(8) |
| C(6)#1-Sn(3)-C(7A)#1 | 91.6(17) | C(6)-Sn(3)-Ag(1) | 76.8(15) |
| C(6A)-Sn(3)-C(7A) | 107.1(14) | C(6)#1-Sn(3)-Ag(1) | 83.9(13) |
| C(6A)#1-Sn(3)-C(7A) | 85.6(14) | C(7A)#1-Sn(3)-Ag(1) | 137.9(6) |
| N(2)-Sn(3)-C(7A) | 106.6(6) | C(7A)-Sn(3)-Ag(1) | 84.3(6) |
| C(7)-Sn(3)-C(7A) | 26.5(9) | Ag(1)#1-Sn(3)-Ag(1) | 53.84(2) |
| C(7)#1-Sn(3)-C(7A) | 112.6(13) | Sn(1)-N(1)-Ge(1)#2 | 117.6(4) |
| C(6)-Sn(3)-C(7A) | 91.6(17) | Sn(1)-N(1)-Sn(1)#2 | 117.6(4) |
| C(6)#1-Sn(3)-C(7A) | 106.1(18) | Ge(1)#2-N(1)-Sn(1)#2 | 0.00(4) |
| C(7A)#1-Sn(3)-C(7A) | 136.4(13) | Sn(1)-N(1)-Ag(1)#2 | 112.66(7) |
| C(6A)-Sn(3)-Ag(1)#1 | 81.4(13) | Ge(1)#2-N(1)-Ag(1)#2 | 109.67(6) |
| C(6A)#1-Sn(3)-Ag(1)#1 | 91.8(13) | Sn(1)#2-N(1)-Ag(1)#2 | 109.67(6) |
| N(2)-Sn(3)-Ag(1)#1 | 36.80(15) | Sn(1)-N(1)-Ag(1) | 109.67(6) |
| C(7)-Sn(3)-Ag(1)#1 | 149.1(8) | Ge(1)#2-N(1)-Ag(1) | 112.66(7) |

| | | | |
|---|---|---|---|
| Sn(1)#2-N(1)-Ag(1) | 112.66(7) | C(5)-C(5A)-C(5A)#1 | 8(5) |
| Ag(1)#2-N(1)-Ag(1) | 91.7(3) | C(5)-C(5A)-Sn(2) | 74(5) |
| Sn(3)-N(2)-Sn(2) | 118.6(4) | C(5A)#1-C(5A)-Sn(2) | 72.7(7) |
| Sn(3)-N(2)-Ag(1)#1 | 110.4(3) | C(6A)#1-C(6)-C(6)#1 | 109(10) |
| Sn(2)-N(2)-Ag(1)#1 | 111.8(3) | C(6A)#1-C(6)-C(6A) | 84(10) |
| Sn(3)-N(2)-Ag(1) | 110.4(3) | C(6)#1-C(6)-C(6A) | 25(5) |
| Sn(2)-N(2)-Ag(1) | 111.8(3) | C(6A)#1-C(6)-Sn(3) | 56(10) |
| Ag(1)#1-N(2)-Ag(1) | 90.2(3) | C(6)#1-C(6)-Sn(3) | 82.3(16) |
| C(1A)-C(1)-Sn(1) | 85.1(18) | C(6A)-C(6)-Sn(3) | 67(7) |
| C(1)-C(1A)-Sn(1) | 66.1(17) | C(6)#1-C(6A)-C(6) | 47(10) |
| C(2A)-C(2)-Sn(1) | 78.5(16) | C(6)#1-C(6A)-C(6A)#1 | 71(10) |
| C(2)-C(2A)-Sn(1) | 68.0(16) | C(6)-C(6A)-C(6A)#1 | 25(5) |
| C(3A)-C(3)-Sn(1) | 72(2) | C(6)#1-C(6A)-Sn(3) | 116(10) |
| C(3)-C(3A)-Sn(1) | 83(2) | C(6)-C(6A)-Sn(3) | 92(7) |
| C(4A)-C(4)-Sn(2) | 59.9(14) | C(6A)#1-C(6A)-Sn(3) | 78.5(13) |
| C(4)-C(4A)-Sn(2) | 81.0(17) | C(7A)-C(7)-Sn(3) | 89(2) |
| C(5A)-C(5)-C(5A)#1 | 163(10) | C(7)-C(7A)-Sn(3) | 65(2) |
| C(5A)-C(5)-Sn(2) | 88(5) | | |
| C(5A)#1-C(5)-Sn(2) | 88(5) | | |

**Table A.34**. Anisotropic displacement parameters ($Å^2$ x $10^3$) for $C_{24}H_{72}N_4Ge_4Sn_4Ag_4$ (**9**).

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Ag(1) | 25(1) | 24(1) | 28(1) | 0(1) | 10(1) | -1(1) |
| Sn(1) | 51(1) | 31(1) | 38(1) | 6(1) | 20(1) | -4(1) |
| Ge(1) | 51(1) | 31(1) | 38(1) | 6(1) | 20(1) | -4(1) |
| Sn(2) | 24(1) | 87(1) | 33(1) | 0 | 14(1) | 0 |
| Ge(2) | 24(1) | 87(1) | 33(1) | 0 | 14(1) | 0 |
| Sn(3) | 29(1) | 72(1) | 28(1) | 0 | 10(1) | 0 |
| Ge(3) | 29(1) | 72(1) | 28(1) | 0 | 10(1) | 0 |
| N(1) | 26(5) | 18(4) | 34(5) | 0 | 6(4) | 0 |
| N(2) | 13(4) | 38(5) | 29(4) | 0 | 10(3) | 0 |

**Table A.35**. Atomic Coordinates (x $10^4$) and Equivalent Isotropic Displacement Parameters (Å x $10^3$) for $C_{24}H_{72}N_4Si_4Ag_4$ (**10**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Ag(1) | 8025(1) | 3568(1) | 1719(1) | 22(1) |
| Ag(2) | 8032(1) | 1408(1) | 1724(1) | 22(1) |
| Si(1) | 10426(1) | 2555(1) | 792(1) | 26(1) |
| Si(2) | 7303(1) | 2391(1) | 195(1) | 27(1) |
| Si(3) | 5978(1) | 5276(1) | 2145(1) | 31(1) |
| Si(4) | 5907(1) | -304(1) | 2232(1) | 24(1) |
| N(1) | 8557(2) | 2490(1) | 924(1) | 21(1) |
| N(2) | 7500 | 4664(2) | 2500 | 22(1) |
| N(3) | 7500 | 301(2) | 2500 | 22(1) |
| C(1) | 11050(3) | 1691(3) | 79(2) | 56(1) |
| C(2) | 10996(3) | 3810(2) | 523(2) | 47(1) |
| C(3) | 11423(3) | 2245(2) | 1656(2) | 36(1) |
| C(4) | 7191(3) | 1118(2) | -145(2) | 47(1) |
| C(5) | 7787(3) | 3183(3) | -592(2) | 50(1) |
| C(6) | 5447(3) | 2762(2) | 484(2) | 37(1) |
| C(7) | 5442(4) | 6313(2) | 2744(2) | 56(1) |
| C(8) | 6318(3) | 5743(2) | 1200(2) | 48(1) |
| C(9) | 4388(3) | 4443(2) | 2080(2) | 45(1) |
| C(10) | 4900(3) | -770(2) | 3041(2) | 38(1) |
| C(11) | 6284(3) | -1349(2) | 1613(2) | 37(1) |

| | | | | | |
|---|---|---|---|---|---|
| | C(12) | 4653(3) | 525(2) | 1721(2) | 34(1) |

**Table A.36**. Interatomic Distances (Å) and Angles (°) for $C_{24}H_{72}N_4Si_4Ag_4$ (**10**).

| | | | |
|---|---|---|---|
| Ag(1)-N(2) | 2.141(2) | Si(4)-C(10) | 1.874(3) |
| Ag(1)-N(1) | 2.1425(19) | N(2)-Si(3)#1 | 1.7487(15) |
| Ag(1)-Ag(2) | 2.9822(6) | N(2)-Ag(1)#1 | 2.141(2) |
| Ag(1)-Ag(1)#1 | 3.0282(6) | N(3)-Si(4)#1 | 1.7485(15) |
| Ag(2)-N(3) | 2.146(2) | N(3)-Ag(2)#1 | 2.146(2) |
| Ag(2)-N(1) | 2.1512(19) | N(2)-Ag(1)-N(1) | 179.01(7) |
| Ag(2)-Ag(2)#1 | 3.0158(6) | N(2)-Ag(1)-Ag(2) | 134.87(5) |
| Si(1)-N(1) | 1.745(2) | N(1)-Ag(1)-Ag(2) | 46.13(5) |
| Si(1)-C(3) | 1.858(3) | N(2)-Ag(1)-Ag(1)#1 | 44.99(5) |
| Si(1)-C(1) | 1.865(3) | N(1)-Ag(1)-Ag(1)#1 | 136.01(5) |
| Si(1)-C(2) | 1.879(3) | Ag(2)-Ag(1)-Ag(1)#1 | 89.879(5) |
| Si(2)-N(1) | 1.748(2) | N(3)-Ag(2)-N(1) | 178.51(7) |
| Si(2)-C(5) | 1.866(3) | N(3)-Ag(2)-Ag(1) | 135.49(5) |
| Si(2)-C(4) | 1.867(3) | N(1)-Ag(2)-Ag(1) | 45.89(5) |
| Si(2)-C(6) | 1.871(3) | N(3)-Ag(2)-Ag(2)#1 | 45.37(5) |
| Si(3)-N(2) | 1.7487(15) | N(1)-Ag(2)-Ag(2)#1 | 136.00(5) |
| Si(3)-C(9) | 1.864(3) | Ag(1)-Ag(2)-Ag(2)#1 | 90.119(5) |
| Si(3)-C(7) | 1.872(3) | N(1)-Si(1)-C(3) | 109.93(11) |
| Si(3)-C(8) | 1.874(3) | N(1)-Si(1)-C(1) | 112.57(13) |
| Si(4)-N(3) | 1.7485(15) | C(3)-Si(1)-C(1) | 106.94(15) |
| Si(4)-C(12) | 1.863(3) | N(1)-Si(1)-C(2) | 111.43(12) |
| Si(4)-C(11) | 1.869(3) | C(3)-Si(1)-C(2) | 107.33(14) |

| | | | |
|---|---|---|---|
| C(1)-Si(1)-C(2) | 108.41(15) | C(11)-Si(4)-C(10) | 108.20(13) |
| N(1)-Si(2)-C(5) | 112.05(12) | Si(1)-N(1)-Si(2) | 122.37(11) |
| N(1)-Si(2)-C(4) | 110.95(12) | Si(1)-N(1)-Ag(1) | 107.40(10) |
| C(5)-Si(2)-C(4) | 107.92(14) | Si(2)-N(1)-Ag(1) | 114.37(10) |
| N(1)-Si(2)-C(6) | 110.91(12) | Si(1)-N(1)-Ag(2) | 111.50(10) |
| C(5)-Si(2)-C(6) | 106.94(14) | Si(2)-N(1)-Ag(2) | 107.94(10) |
| C(4)-Si(2)-C(6) | 107.87(14) | Ag(1)-N(1)-Ag(2) | 87.98(7) |
| N(2)-Si(3)-C(9) | 110.30(13) | Si(3)#1-N(2)-Si(3) | 122.14(17) |
| N(2)-Si(3)-C(7) | 111.89(14) | Si(3)#1-N(2)-Ag(1) | 113.45(4) |
| C(9)-Si(3)-C(7) | 106.96(15) | Si(3)-N(2)-Ag(1) | 106.62(4) |
| N(2)-Si(3)-C(8) | 111.03(10) | Si(3)#1-N(2)-Ag(1)#1 | 106.62(4) |
| C(9)-Si(3)-C(8) | 107.48(15) | Si(3)-N(2)-Ag(1)#1 | 113.45(4) |
| C(7)-Si(3)-C(8) | 109.00(15) | Ag(1)-N(2)-Ag(1)#1 | 90.03(11) |
| N(3)-Si(4)-C(12) | 110.68(12) | Si(4)-N(3)-Si(4)#1 | 122.87(17) |
| N(3)-Si(4)-C(11) | 111.88(11) | Si(4)-N(3)-Ag(2)#1 | 108.82(4) |
| C(12)-Si(4)-C(11) | 107.05(13) | Si(4)#1-N(3)-Ag(2)#1 | 110.98(4) |
| N(3)-Si(4)-C(10) | 111.73(10) | Si(4)-N(3)-Ag(2) | 110.98(4) |
| C(12)-Si(4)-C(10) | 107.07(13) | Si(4)#1-N(3)-Ag(2) | 108.82(4) |
| | | Ag(2)#1-N(3)-Ag(2) | 89.26(11) |

**Table A.37**. Anisotropic displacement parameters ($Å^2$ x $10^3$) for $C_{24}H_{72}N_4Si_4Ag_4$ (**10**).

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Ag(1) | 23(1) | 20(1) | 22(1) | -1(1) | 3(1) | 2(1) |
| Ag(2) | 25(1) | 20(1) | 20(1) | 2(1) | 0(1) | 0(1) |
| Si(1) | 22(1) | 32(1) | 23(1) | -2(1) | 4(1) | 2(1) |
| Si(2) | 26(1) | 36(1) | 20(1) | 2(1) | -2(1) | 1(1) |
| Si(3) | 32(1) | 26(1) | 35(1) | 6(1) | 10(1) | 8(1) |
| Si(4) | 26(1) | 21(1) | 26(1) | -1(1) | -1(1) | -2(1) |
| N(1) | 22(1) | 25(1) | 17(1) | 3(1) | 1(1) | 1(1) |
| N(2) | 25(2) | 17(2) | 24(2) | 0 | 9(1) | 0 |
| N(3) | 25(2) | 20(2) | 21(2) | 0 | -2(1) | 0 |
| C(1) | 37(2) | 83(3) | 49(2) | -27(2) | 7(2) | 10(2) |
| C(2) | 36(2) | 53(2) | 50(2) | 21(2) | 1(2) | -11(2) |
| C(3) | 27(2) | 41(2) | 41(2) | 5(1) | -3(1) | 4(1) |
| C(4) | 48(2) | 53(2) | 38(2) | -14(2) | -9(1) | -1(2) |
| C(5) | 43(2) | 75(3) | 31(2) | 18(2) | -2(1) | -1(2) |
| C(6) | 30(2) | 43(2) | 37(2) | 5(1) | -3(1) | 2(1) |
| C(7) | 60(2) | 41(2) | 67(3) | 2(2) | 25(2) | 20(2) |
| C(8) | 49(2) | 48(2) | 48(2) | 20(2) | 9(2) | 11(2) |
| C(9) | 30(2) | 56(2) | 48(2) | 12(2) | 5(1) | 5(2) |
| C(10) | 36(2) | 40(2) | 37(2) | 4(1) | 2(1) | -5(1) |
| C(11) | 43(2) | 28(2) | 40(2) | -7(1) | -4(1) | -3(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(12) | 34(2) | 33(2) | 37(2) | 1(1) | -7(1) | -1(1) |

**Table A.38**. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å $^2$ x $10^3$) for $C_{24}H_{72}N_4Si_8Ag_4$ (**10**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 10773 | 1052 | 207 | 84(8) |
| H(1B) | 12078 | 1725 | 47 | 84(8) |
| H(1C) | 10618 | 1857 | -382 | 84(8) |
| H(2A) | 10521 | 3985 | 75 | 82(7) |
| H(2B) | 12018 | 3826 | 463 | 82(7) |
| H(2C) | 10736 | 4255 | 896 | 82(7) |
| H(3A) | 11007 | 2585 | 2053 | 70(7) |
| H(3B) | 12414 | 2425 | 1617 | 70(7) |
| H(3C) | 11358 | 1568 | 1741 | 70(7) |
| H(4A) | 8087 | 943 | -358 | 74(7) |
| H(4B) | 6431 | 1067 | -503 | 74(7) |
| H(4C) | 7000 | 696 | 252 | 74(7) |
| H(5A) | 7858 | 3835 | -431 | 63(6) |
| H(5B) | 7057 | 3133 | -966 | 63(6) |
| H(5C) | 8693 | 2982 | -780 | 63(6) |
| H(6A) | 5196 | 2415 | 912 | 59(6) |
| H(6B) | 4762 | 2622 | 101 | 59(6) |
| H(6C) | 5439 | 3437 | 584 | 59(6) |
| H(7A) | 5214 | 6076 | 3216 | 82(7) |
| H(7B) | 4616 | 6628 | 2533 | 82(7) |
| H(7C) | 6225 | 6759 | 2785 | 82(7) |

| | | | | |
|---|---|---|---|---|
| H(8A) | 7056 | 6224 | 1222 | 86(8) |
| H(8B) | 5449 | 6017 | 1000 | 86(8) |
| H(8C) | 6621 | 5224 | 897 | 86(8) |
| H(9A) | 4677 | 3848 | 1866 | 56(6) |
| H(9B) | 3644 | 4731 | 1785 | 56(6) |
| H(9C) | 4033 | 4326 | 2557 | 56(6) |
| H(10A) | 5459 | -1261 | 3279 | 53(5) |
| H(10B) | 3994 | -1033 | 2880 | 53(5) |
| H(10C) | 4737 | -254 | 3373 | 53(5) |
| H(11A) | 6691 | -1117 | 1173 | 59(6) |
| H(11B) | 5403 | -1681 | 1502 | 59(6) |
| H(11C) | 6949 | -1779 | 1850 | 59(6) |
| H(12A) | 4554 | 1112 | 1987 | 49(5) |
| H(12B) | 3729 | 226 | 1662 | 49(5) |
| H(12C) | 5036 | 662 | 1253 | 49(5) |

**Table A.39**. Atomic Coordinates (x $10^4$) and Equivalent Isotropic Displacement Parameters (Å x $10^3$) for $C_{28}H_{76}N_2O_4Cl_4Sn_4Zn_2$ (**11**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Sn(1) | 2396(1) | 5556(1) | 4881(1) | 38(1) |
| Sn(2) | -368(1) | 7027(1) | 6018(1) | 43(1) |
| Sn(3) | -1999(1) | 8739(1) | 10070(1) | 44(1) |
| Sn(4) | -2937(1) | 8342(1) | 8752(1) | 43(1) |
| Zn(1) | 543(1) | 4019(1) | 5396(1) | 32(1) |
| Zn(2) | -4952(1) | 11020(1) | 9682(1) | 31(1) |
| Cl(1) | 2630(3) | 2374(3) | 5131(1) | 44(1) |
| Cl(2) | -97(3) | 3323(3) | 6418(1) | 50(1) |
| Cl(3) | -4358(4) | 12515(3) | 9825(2) | 59(1) |
| Cl(4) | -5479(3) | 11698(3) | 8653(1) | 44(1) |
| N(1) | 569(8) | 5700(8) | 5265(4) | 33(2) |
| N(2) | -3621(9) | 9203(8) | 9676(4) | 37(2) |
| C(1) | 3358(12) | 4592(12) | 3977(5) | 47(3) |
| C(2) | 2175(14) | 7423(12) | 4681(6) | 59(4) |
| C(3) | 3662(12) | 4608(12) | 5563(6) | 55(4) |
| C(4) | -1029(16) | 8893(12) | 5628(8) | 81(5) |
| C(5) | -1886(14) | 6845(15) | 6699(6) | 71(4) |
| C(6) | 950(15) | 6809(13) | 6633(6) | 65(4) |
| C(7) | -2342(14) | 9838(14) | 10871(6) | 65(4) |
| C(8) | -589(15) | 9045(16) | 9318(7) | 77(5) |

| | | | | |
|---|---|---|---|---|
| C(9) | -1236(14) | 6823(13) | 10389(7) | 73(4) |
| C(10) | -1336(16) | 6484(12) | 8771(7) | 77(5) |
| C(11) | -2221(14) | 9412(14) | 8049(6) | 67(4) |
| C(12) | -4338(14) | 8073(13) | 8434(6) | 65(4) |
| Li(1) | 2120(20) | 1758(18) | 6240(12) | 58(6) |
| Li(2) | -5250(20) | 6830(20) | 11252(11) | 62(7) |
| O(1) | 2269(14) | 48(10) | 6373(6) | 119(5) |
| C(13) | 2550(80) | -630(80) | 6990(40) | 110(30) |
| C(13') | 1090(30) | -30(30) | 6976(18) | 137(11) |
| C(14) | 1410(40) | -280(40) | 7514(13) | 270(20) |
| C(15) | 2820(40) | -1010(30) | 6044(19) | 119(19) |
| C(15') | 3830(50) | -1240(50) | 5440(20) | 73(13) |
| C(16) | 3960(60) | -860(40) | 5610(40) | 150(30) |
| C(16') | 3810(90) | -1600(90) | 5860(50) | 230(40) |
| O(2) | 3041(10) | 1975(10) | 6789(5) | 83(3) |
| C(17) | 4700(40) | 1320(40) | 6466(17) | 84(10) |
| C(17') | 4190(50) | 810(50) | 6980(20) | 133(16) |
| C(18) | 5280(30) | 280(30) | 6668(18) | 201(15) |
| C(19) | 2710(30) | 2990(30) | 7224(12) | 169(12) |
| C(20) | 1640(20) | 3370(20) | 7680(11) | 130(9) |
| O(3) | -3911(11) | 5089(9) | 11277(5) | 77(3) |
| C(21') | -2650(60) | 4540(60) | 10870(30) | 170(20) |
| C(21) | -3610(30) | 4190(30) | 10749(15) | 68(8) |

| | | | | |
|---|---|---|---|---|
| C(22) | -2580(20) | 4170(20) | 10205(11) | 132(8) |
| C(23) | -4230(60) | 4030(60) | 11500(30) | 170(20) |
| C(23') | -2980(40) | 4660(40) | 11660(20) | 112(13) |
| C(24) | -3340(40) | 3640(40) | 12120(20) | 269(19) |
| O(4) | -6789(12) | 6873(14) | 11841(6) | 109(4) |
| C(25) | -7220(20) | 7200(20) | 12534(10) | 126(9) |
| C(26) | -6250(20) | 7250(20) | 12802(9) | 121(8) |
| C(27) | -7560(40) | 6080(30) | 11570(17) | 236(19) |
| C(28) | -8300(30) | 7140(30) | 11490(16) | 214(18) |

**Table A.40**. Interatomic Distances (Å) and Angles (°) for $C_{28}H_{76}N_2O_4Cl_4Sn_4Zn_2$ (**11**).

| | | | |
|---|---|---|---|
| Sn(1)-N(1) | 2.078(8) | Zn(2)-N(2) | 2.006(9) |
| Sn(1)-C(1) | 2.108(11) | Zn(2)-N(2)#2 | 2.018(8) |
| Sn(1)-C(2) | 2.140(12) | Zn(2)-Cl(3) | 2.297(3) |
| Sn(1)-C(3) | 2.159(12) | Zn(2)-Cl(4) | 2.339(3) |
| Sn(2)-N(1) | 2.079(8) | Zn(2)-Zn(2)#2 | 2.698(2) |
| Sn(2)-C(5) | 2.116(13) | Zn(2)-Li(2)#2 | 3.134(18) |
| Sn(2)-C(4) | 2.134(13) | Cl(1)-Li(1) | 2.38(2) |
| Sn(2)-C(6) | 2.171(14) | Cl(2)-Li(1) | 2.39(2) |
| Sn(3)-C(7) | 2.094(13) | Cl(3)-Li(2)#2 | 2.38(2) |
| Sn(3)-N(2) | 2.097(10) | Cl(4)-Li(2)#2 | 2.36(2) |
| Sn(3)-C(9) | 2.135(14) | N(1)-Zn(1)#1 | 2.036(9) |
| Sn(3)-C(8) | 2.162(13) | N(2)-Zn(2)#2 | 2.018(8) |
| Sn(4)-N(2) | 2.094(8) | Li(1)-O(2) | 1.88(3) |
| Sn(4)-C(12) | 2.113(14) | Li(1)-O(1) | 1.97(2) |
| Sn(4)-C(11) | 2.141(12) | Li(2)-O(4) | 1.95(2) |
| Sn(4)-C(10) | 2.155(14) | Li(2)-O(3) | 1.95(3) |
| Zn(1)-N(1) | 2.027(8) | Li(2)-Cl(4)#2 | 2.36(2) |
| Zn(1)-N(1)#1 | 2.036(9) | Li(2)-Cl(3)#2 | 2.38(2) |
| Zn(1)-Cl(2) | 2.301(3) | Li(2)-Zn(2)#2 | 3.134(18) |
| Zn(1)-Cl(1) | 2.322(3) | O(1)-C(15) | 1.31(3) |
| Zn(1)-Zn(1)#1 | 2.695(2) | O(1)-C(13) | 1.47(9) |
| Zn(1)-Li(1) | 3.12(2) | O(1)-C(13') | 1.69(4) |

| | | | |
|---|---|---|---|
| C(13)-C(14) | 1.45(8) | C(21')-C(23') | 1.61(7) |
| C(13)-C(13') | 1.56(9) | C(21)-C(22) | 1.46(3) |
| C(13)-C(15) | 2.00(9) | C(21)-C(23) | 1.60(6) |
| C(13')-C(14) | 1.23(4) | C(23)-C(24) | 1.76(6) |
| C(15)-C(16') | 1.05(9) | C(23')-C(24) | 1.63(5) |
| C(15)-C(15') | 1.48(5) | O(4)-C(25) | 1.45(2) |
| C(15)-C(16) | 1.52(7) | O(4)-C(27) | 1.82(4) |
| C(15')-C(16) | 0.70(7) | C(25)-C(26) | 1.43(3) |
| C(15')-C(16') | 0.94(9) | C(27)-C(28) | 1.18(3) |
| C(16)-C(16') | 1.05(9) | N(1)-Sn(1)-C(1) | 115.6(4) |
| O(2)-C(19) | 1.45(3) | N(1)-Sn(1)-C(2) | 107.8(4) |
| O(2)-C(17') | 1.53(6) | C(1)-Sn(1)-C(2) | 105.0(5) |
| O(2)-C(17) | 1.74(4) | N(1)-Sn(1)-C(3) | 110.8(4) |
| C(17)-C(18) | 1.19(4) | C(1)-Sn(1)-C(3) | 106.8(5) |
| C(17)-C(17') | 1.35(5) | C(2)-Sn(1)-C(3) | 110.8(5) |
| C(17')-C(18) | 1.20(5) | N(1)-Sn(2)-C(5) | 114.7(5) |
| C(19)-C(20) | 1.32(3) | N(1)-Sn(2)-C(4) | 110.8(5) |
| O(3)-C(23') | 1.40(5) | C(5)-Sn(2)-C(4) | 110.8(6) |
| O(3)-C(21') | 1.42(6) | N(1)-Sn(2)-C(6) | 110.7(4) |
| O(3)-C(23) | 1.49(6) | C(5)-Sn(2)-C(6) | 102.8(5) |
| O(3)-C(21) | 1.50(3) | C(4)-Sn(2)-C(6) | 106.5(6) |
| C(21')-C(22) | 1.48(6) | C(7)-Sn(3)-N(2) | 115.3(4) |
| C(21')-C(21) | 1.48(7) | C(7)-Sn(3)-C(9) | 107.2(6) |

| | | | |
|---|---|---|---|
| N(2)-Sn(3)-C(9) | 109.4(5) | Cl(1)-Zn(1)-Li(1) | 49.3(4) |
| C(7)-Sn(3)-C(8) | 105.4(6) | Zn(1)#1-Zn(1)-Li(1) | 172.9(4) |
| N(2)-Sn(3)-C(8) | 108.2(5) | N(2)-Zn(2)-N(2)#2 | 95.8(4) |
| C(9)-Sn(3)-C(8) | 111.4(6) | N(2)-Zn(2)-Cl(3) | 117.8(3) |
| N(2)-Sn(4)-C(12) | 113.0(4) | N(2)#2-Zn(2)-Cl(3) | 122.4(3) |
| N(2)-Sn(4)-C(11) | 109.7(4) | N(2)-Zn(2)-Cl(4) | 112.3(3) |
| C(12)-Sn(4)-C(11) | 111.1(6) | N(2)#2-Zn(2)-Cl(4) | 111.8(3) |
| N(2)-Sn(4)-C(10) | 110.9(5) | Cl(3)-Zn(2)-Cl(4) | 97.44(11) |
| C(12)-Sn(4)-C(10) | 105.2(6) | N(2)-Zn(2)-Zn(2)#2 | 48.1(2) |
| C(11)-Sn(4)-C(10) | 106.6(6) | N(2)#2-Zn(2)-Zn(2)#2 | 47.7(3) |
| N(1)-Zn(1)-N(1)#1 | 96.9(3) | Cl(3)-Zn(2)-Zn(2)#2 | 138.40(11) |
| N(1)-Zn(1)-Cl(2) | 122.1(3) | Cl(4)-Zn(2)-Zn(2)#2 | 124.11(10) |
| N(1)#1-Zn(1)-Cl(2) | 115.6(2) | N(2)-Zn(2)-Li(2)#2 | 127.4(5) |
| N(1)-Zn(1)-Cl(1) | 110.4(3) | N(2)#2-Zn(2)-Li(2)#2 | 135.9(5) |
| N(1)#1-Zn(1)-Cl(1) | 114.3(3) | Cl(3)-Zn(2)-Li(2)#2 | 49.2(5) |
| Cl(2)-Zn(1)-Cl(1) | 98.36(11) | Cl(4)-Zn(2)-Li(2)#2 | 48.4(5) |
| N(1)-Zn(1)-Zn(1)#1 | 48.6(3) | Zn(2)#2-Zn(2)-Li(2)#2 | 171.3(4) |
| N(1)#1-Zn(1)-Zn(1)#1 | 48.3(2) | Zn(1)-Cl(1)-Li(1) | 83.1(5) |
| Cl(2)-Zn(1)-Zn(1)#1 | 136.63(11) | Zn(1)-Cl(2)-Li(1) | 83.4(5) |
| Cl(1)-Zn(1)-Zn(1)#1 | 124.97(10) | Zn(2)-Cl(3)-Li(2)#2 | 84.0(5) |
| N(1)-Zn(1)-Li(1) | 126.9(5) | Zn(2)-Cl(4)-Li(2)#2 | 83.7(6) |
| N(1)#1-Zn(1)-Li(1) | 135.7(5) | Zn(1)-N(1)-Zn(1)#1 | 83.1(3) |
| Cl(2)-Zn(1)-Li(1) | 49.5(4) | Zn(1)-N(1)-Sn(1) | 114.0(4) |

| | | | |
|---|---|---|---|
| Zn(1)#1-N(1)-Sn(1) | 116.3(4) | O(4)-Li(2)-Cl(3)#2 | 110.3(13) |
| Zn(1)-N(1)-Sn(2) | 120.0(4) | O(3)-Li(2)-Cl(3)#2 | 112.6(11) |
| Zn(1)#1-N(1)-Sn(2) | 112.9(4) | Cl(4)#2-Li(2)-Cl(3)#2 | 94.6(6) |
| Sn(1)-N(1)-Sn(2) | 108.9(4) | O(4)-Li(2)-Zn(2)#2 | 127.4(11) |
| Zn(2)-N(2)-Zn(2)#2 | 84.2(4) | O(3)-Li(2)-Zn(2)#2 | 127.2(9) |
| Zn(2)-N(2)-Sn(4) | 114.0(4) | Cl(4)#2-Li(2)-Zn(2)#2 | 47.9(3) |
| Zn(2)#2-N(2)-Sn(4) | 118.9(4) | Cl(3)#2-Li(2)-Zn(2)#2 | 46.8(3) |
| Zn(2)-N(2)-Sn(3) | 118.1(4) | C(15)-O(1)-C(13) | 92(4) |
| Zn(2)#2-N(2)-Sn(3) | 113.5(4) | C(15)-O(1)-C(13') | 106.1(18) |
| Sn(4)-N(2)-Sn(3) | 107.2(4) | C(13)-O(1)-C(13') | 59(3) |
| O(2)-Li(1)-O(1) | 109.0(11) | C(15)-O(1)-Li(1) | 138.1(17) |
| O(2)-Li(1)-Cl(1) | 112.8(11) | C(13)-O(1)-Li(1) | 120(3) |
| O(1)-Li(1)-Cl(1) | 116.5(12) | C(13')-O(1)-Li(1) | 113.5(15) |
| O(2)-Li(1)-Cl(2) | 112.6(11) | C(14)-C(13)-O(1) | 113(6) |
| O(1)-Li(1)-Cl(2) | 111.0(11) | C(14)-C(13)-C(13') | 48(3) |
| Cl(1)-Li(1)-Cl(2) | 94.3(7) | O(1)-C(13)-C(13') | 68(4) |
| O(2)-Li(1)-Zn(1) | 119.5(9) | C(14)-C(13)-C(15) | 130(6) |
| O(1)-Li(1)-Zn(1) | 131.4(12) | O(1)-C(13)-C(15) | 41(3) |
| Cl(1)-Li(1)-Zn(1) | 47.6(4) | C(13')-C(13)-C(15) | 84(4) |
| Cl(2)-Li(1)-Zn(1) | 47.1(4) | C(14)-C(13')-C(13) | 61(4) |
| O(4)-Li(2)-O(3) | 104.9(10) | C(14)-C(13')-O(1) | 112(3) |
| O(4)-Li(2)-Cl(4)#2 | 121.4(12) | C(13)-C(13')-O(1) | 54(3) |
| O(3)-Li(2)-Cl(4)#2 | 112.9(12) | C(13')-C(14)-C(13) | 70(4) |

| | | | |
|---|---|---|---|
| C(16')-C(15)-O(1) | 130(7) | C(17')-O(2)-Li(1) | 118(2) |
| C(16')-C(15)-C(15') | 39(5) | C(17)-O(2)-Li(1) | 113.3(14) |
| O(1)-C(15)-C(15') | 122(3) | C(18)-C(17)-C(17') | 56(3) |
| C(16')-C(15)-C(16) | 44(5) | C(18)-C(17)-O(2) | 112(3) |
| O(1)-C(15)-C(16) | 98(3) | C(17')-C(17)-O(2) | 57(3) |
| C(15')-C(15)-C(16) | 27(3) | C(18)-C(17')-C(17) | 56(3) |
| C(16')-C(15)-C(13) | 110(8) | C(18)-C(17')-O(2) | 128(4) |
| O(1)-C(15)-C(13) | 47(3) | C(17)-C(17')-O(2) | 74(3) |
| C(15')-C(15)-C(13) | 138(4) | C(17)-C(18)-C(17') | 68(3) |
| C(16)-C(15)-C(13) | 113(4) | C(20)-C(19)-O(2) | 119(3) |
| C(16)-C(15')-C(16') | 78(8) | C(23')-O(3)-C(21') | 70(3) |
| C(16)-C(15')-C(15) | 80(8) | C(23')-O(3)-C(23) | 92(3) |
| C(16')-C(15')-C(15) | 45(6) | C(21')-O(3)-C(23) | 106(3) |
| C(15')-C(16)-C(16') | 61(7) | C(23')-O(3)-C(21) | 114(2) |
| C(15')-C(16)-C(15) | 73(8) | C(21')-O(3)-C(21) | 61(3) |
| C(16')-C(16)-C(15) | 44(6) | C(23)-O(3)-C(21) | 65(2) |
| C(15')-C(16')-C(16) | 41(6) | C(23')-O(3)-Li(2) | 124(2) |
| C(15')-C(16')-C(15) | 96(9) | C(21')-O(3)-Li(2) | 127(3) |
| C(16)-C(16')-C(15) | 93(9) | C(23)-O(3)-Li(2) | 122(3) |
| C(19)-O(2)-C(17') | 108(2) | C(21)-O(3)-Li(2) | 119.9(15) |
| C(19)-O(2)-C(17) | 107.1(19) | O(3)-C(21')-C(22) | 115(4) |
| C(17')-O(2)-C(17) | 48(2) | O(3)-C(21')-C(21) | 62(3) |
| C(19)-O(2)-Li(1) | 132.1(16) | C(22)-C(21')-C(21) | 59(3) |

| | | | |
|---|---|---|---|
| O(3)-C(21')-C(23') | 55(3) | O(3)-C(23)-C(24) | 91(3) |
| C(22)-C(21')-C(23') | 161(5) | C(21)-C(23)-C(24) | 122(4) |
| C(21)-C(21')-C(23') | 103(4) | O(3)-C(23')-C(21') | 56(3) |
| C(22)-C(21)-C(21') | 60(3) | O(3)-C(23')-C(24) | 100(3) |
| C(22)-C(21)-O(3) | 111(2) | C(21')-C(23')-C(24) | 120(4) |
| C(21')-C(21)-O(3) | 57(3) | C(23')-C(24)-C(23) | 75(3) |
| C(22)-C(21)-C(23) | 155(3) | C(25)-O(4)-C(27) | 114.4(17) |
| C(21')-C(21)-C(23) | 98(4) | C(25)-O(4)-Li(2) | 126.5(15) |
| O(3)-C(21)-C(23) | 57(2) | C(27)-O(4)-Li(2) | 117.3(17) |
| C(21)-C(22)-C(21') | 60(3) | C(26)-C(25)-O(4) | 112.9(15) |
| O(3)-C(23)-C(21) | 58(2) | C(28)-C(27)-O(4) | 80(3) |

**Table A.41**. Anisotropic displacement parameters ($Å^2$ x $10^3$) for $C_{28}H_{76}N_2O_4Cl_4Sn_4Zn_2$ (**11**).

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Sn(1) | 39(1) | 42(1) | 39(1) | 6(1) | -8(1) | -23(1) |
| Sn(2) | 48(1) | 34(1) | 44(1) | -8(1) | -5(1) | -16(1) |
| Sn(3) | 35(1) | 45(1) | 50(1) | 5(1) | -11(1) | -17(1) |
| Sn(4) | 48(1) | 38(1) | 36(1) | -6(1) | 2(1) | -17(1) |
| Zn(1) | 32(1) | 27(1) | 33(1) | 6(1) | -7(1) | -12(1) |
| Zn(2) | 38(1) | 29(1) | 29(1) | 5(1) | -6(1) | -18(1) |
| Cl(1) | 38(2) | 34(2) | 43(2) | 5(1) | -4(1) | -8(1) |
| Cl(2) | 45(2) | 57(2) | 40(2) | 18(2) | -7(1) | -21(2) |
| Cl(3) | 97(3) | 54(2) | 58(2) | 17(2) | -34(2) | -56(2) |
| Cl(4) | 54(2) | 51(2) | 32(2) | 12(1) | -13(1) | -29(2) |
| N(1) | 33(5) | 23(5) | 37(5) | 2(4) | -2(4) | -12(4) |
| N(2) | 51(6) | 32(5) | 32(5) | -3(4) | 0(4) | -24(5) |
| C(1) | 44(8) | 53(8) | 43(7) | 4(6) | -6(6) | -23(7) |
| C(2) | 71(10) | 65(9) | 54(8) | 17(7) | -19(7) | -44(8) |
| C(3) | 38(8) | 65(9) | 70(9) | -3(7) | -19(7) | -27(7) |
| C(4) | 93(13) | 29(8) | 107(13) | -8(8) | -14(10) | -18(8) |
| C(5) | 57(9) | 94(12) | 58(9) | -29(8) | 15(7) | -37(9) |
| C(6) | 80(11) | 62(9) | 57(8) | -12(7) | -13(8) | -33(9) |
| C(7) | 60(10) | 80(11) | 65(9) | 3(8) | -34(8) | -31(9) |
| C(8) | 63(10) | 92(12) | 79(11) | 4(9) | -6(8) | -43(10) |
| C(9) | 58(10) | 56(9) | 69(10) | 3(8) | -6(8) | -2(8) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(10) | 94(12) | 41(8) | 63(9) | -18(7) | -7(9) | -7(9) |
| C(11) | 74(10) | 81(11) | 34(7) | -15(7) | 16(7) | -38(9) |
| C(12) | 63(10) | 66(10) | 52(8) | -21(7) | -2(7) | -18(8) |
| Li(1) | 46(13) | 26(11) | 78(15) | 21(10) | -10(11) | -2(10) |
| Li(2) | 68(16) | 54(14) | 61(14) | 17(11) | 18(12) | -43(13) |
| O(1) | 158(13) | 55(7) | 90(9) | 11(7) | 22(8) | -29(8) |
| C(14) | 320(50) | 380(60) | 72(18) | -20(30) | 0(20) | -150(50) |
| C(15) | 120(30) | 70(20) | 150(30) | -100(20) | 120(30) | -70(20) |
| C(16) | 160(50) | 60(30) | 160(50) | -40(30) | 60(40) | -30(30) |
| O(2) | 72(7) | 77(7) | 75(7) | -5(6) | -36(6) | -5(6) |
| C(18) | 86(18) | 140(30) | 300(40) | -90(30) | 0(20) | 18(17) |
| C(19) | 240(40) | 170(30) | 120(20) | -40(20) | -40(20) | -100(30) |
| C(20) | 89(16) | 150(20) | 115(17) | -47(16) | -4(13) | -31(16) |
| O(3) | 85(8) | 46(6) | 98(8) | 8(6) | -30(7) | -27(6) |
| C(22) | 111(18) | 170(20) | 132(18) | -45(16) | 17(14) | -83(17) |
| O(4) | 89(9) | 160(13) | 100(9) | 46(9) | -13(7) | -88(10) |
| C(25) | 106(17) | 160(20) | 103(16) | 40(14) | 32(13) | -85(16) |
| C(26) | 125(19) | 200(20) | 77(13) | 33(13) | -5(12) | -118(19) |
| C(27) | 290(50) | 130(30) | 220(40) | 0(30) | -140(30) | 0(30) |
| C(28) | 160(30) | 120(20) | 210(30) | 20(20) | 10(20) | 30(20) |

**Table A.42**. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å $^2$ x $10^3$) for $C_{28}H_{76}N_2O_4Cl_4Sn_4Zn_2$ (**11**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 3493 | 3739 | 4032 | 40(18) |
| H(1B) | 4178 | 4595 | 3834 | 40(18) |
| H(1C) | 2839 | 5005 | 3654 | 40(18) |
| H(2A) | 1813 | 7744 | 4296 | 50(20) |
| H(2B) | 3005 | 7404 | 4607 | 50(20) |
| H(2C) | 1607 | 7958 | 5049 | 50(20) |
| H(3A) | 3699 | 5222 | 5801 | 80(30) |
| H(3B) | 4515 | 4063 | 5324 | 80(30) |
| H(3C) | 3335 | 4118 | 5865 | 80(30) |
| H(4A) | -524 | 8871 | 5194 | 80(30) |
| H(4B) | -936 | 9412 | 5907 | 80(30) |
| H(4C) | -1923 | 9235 | 5607 | 80(30) |
| H(5A) | -2651 | 7216 | 6518 | 100(30) |
| H(5B) | -2060 | 7269 | 7101 | 100(30) |
| H(5C) | -1636 | 5969 | 6787 | 100(30) |
| H(6A) | 1389 | 5941 | 6758 | 100(30) |
| H(6B) | 470 | 7319 | 7021 | 100(30) |
| H(6C) | 1574 | 7071 | 6393 | 100(30) |
| H(7A) | -2768 | 10714 | 10759 | 60(20) |
| H(7B) | -1533 | 9639 | 10979 | 60(20) |
| H(7C) | -2881 | 9664 | 11243 | 60(20) |

| | | | | |
|---|---|---|---|---|
| H(8A) | -162 | 8365 | 9006 | 100(30) |
| H(8B) | 38 | 9079 | 9517 | 100(30) |
| H(8C) | -1018 | 9826 | 9097 | 100(30) |
| H(9A) | -1782 | 6479 | 10331 | 100(30) |
| H(9B) | -1205 | 6784 | 10846 | 100(30) |
| H(9C) | -379 | 6345 | 10135 | 100(30) |
| H(10A) | -571 | 6552 | 8773 | 90(30) |
| H(10B) | -1193 | 6022 | 8389 | 90(30) |
| H(10C) | -1531 | 6050 | 9160 | 90(30) |
| H(11A) | -2372 | 10157 | 8255 | 100(30) |
| H(11B) | -2662 | 9647 | 7690 | 100(30) |
| H(11C) | -1309 | 8911 | 7886 | 100(30) |
| H(12A) | -4800 | 7790 | 8796 | 80(30) |
| H(12B) | -3917 | 7453 | 8090 | 80(30) |
| H(12C) | -4935 | 8855 | 8270 | 80(30) |

**Table A.43**. Atomic Coordinates (x $10^4$) and Equivalent Isotropic Displacement Parameters (Å x $10^3$) for $C_{26}H_{38}N_2Sn_2Zr_2$ (**12**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Sn(1) | 6936(1) | 1621(1) | 3866(1) | 36(1) |
| Zr(1) | 5741(1) | 227(1) | 6439(1) | 33(1) |
| C(1) | 3279(8) | 844(4) | 7334(7) | 58(2) |
| C(2) | 3742(8) | 1449(4) | 6562(7) | 58(2) |
| C(3) | 5278(9) | 1755(4) | 7134(6) | 53(2) |
| C(4) | 5714(8) | 1339(4) | 8278(6) | 53(2) |
| C(5) | 4485(9) | 766(4) | 8422(7) | 62(2) |
| C(6) | 8610(7) | -357(4) | 6481(8) | 56(2) |
| C(7) | 7727(7) | -1012(4) | 6832(6) | 50(2) |
| C(8) | 7328(8) | -878(4) | 8051(7) | 58(2) |
| C(9) | 8005(9) | -139(5) | 8497(8) | 64(2) |
| C(10) | 8769(8) | 203(4) | 7499(8) | 64(2) |
| C(11) | 9133(7) | 1918(4) | 5148(6) | 54(2) |
| C(12) | 5360(8) | 2679(4) | 3854(6) | 54(2) |
| C(13) | 7428(7) | 1366(4) | 1925(5) | 46(1) |
| N(1) | 5873(5) | 604(2) | 4559(4) | 34(1) |

**Table A.44**. Interatomic Distances (Å) and Angles (°) for $C_{26}H_{38}N_2Sn_2Zr_2$ (**12**).

| | | | |
|---|---|---|---|
| Sn(1)-N(1) | 2.047(4) | C(6)-C(10) | 1.382(10) |
| Sn(1)-C(11) | 2.136(6) | C(7)-C(8) | 1.367(9) |
| Sn(1)-C(13) | 2.146(6) | C(8)-C(9) | 1.373(9) |
| Sn(1)-C(12) | 2.152(6) | C(9)-C(10) | 1.402(10) |
| Zr(1)-N(1) | 2.057(4) | N(1)-Zr(1)#1 | 2.060(4) |
| Zr(1)-N(1)#1 | 2.060(4) | N(1)-Sn(1)-C(11) | 109.4(2) |
| Zr(1)-C(6) | 2.545(6) | N(1)-Sn(1)-C(13) | 108.85(19) |
| Zr(1)-C(1) | 2.559(6) | C(11)-Sn(1)-C(13) | 111.3(2) |
| Zr(1)-C(10) | 2.576(6) | N(1)-Sn(1)-C(12) | 110.8(2) |
| Zr(1)-C(5) | 2.584(7) | C(11)-Sn(1)-C(12) | 106.3(2) |
| Zr(1)-C(7) | 2.586(6) | C(13)-Sn(1)-C(12) | 110.3(2) |
| Zr(1)-C(2) | 2.595(6) | N(1)-Zr(1)-N(1)#1 | 80.95(17) |
| Zr(1)-C(4) | 2.625(6) | N(1)-Zr(1)-C(6) | 87.0(2) |
| Zr(1)-C(3) | 2.626(6) | N(1)#1-Zr(1)-C(6) | 107.20(19) |
| Zr(1)-C(8) | 2.657(6) | N(1)-Zr(1)-C(1) | 112.5(2) |
| Zr(1)-C(9) | 2.682(7) | N(1)#1-Zr(1)-C(1) | 87.06(19) |
| C(1)-C(2) | 1.356(9) | C(6)-Zr(1)-C(1) | 157.8(2) |
| C(1)-C(5) | 1.392(9) | N(1)-Zr(1)-C(10) | 102.8(2) |
| C(2)-C(3) | 1.408(9) | N(1)#1-Zr(1)-C(10) | 135.8(2) |
| C(3)-C(4) | 1.363(9) | C(6)-Zr(1)-C(10) | 31.3(2) |
| C(4)-C(5) | 1.400(9) | C(1)-Zr(1)-C(10) | 128.6(3) |
| C(6)-C(7) | 1.367(9) | N(1)-Zr(1)-C(5) | 137.17(19) |

| | | | |
|---|---|---|---|
| N(1)#1-Zr(1)-C(5) | 108.3(2) | C(7)-Zr(1)-C(4) | 119.6(2) |
| C(6)-Zr(1)-C(5) | 126.5(2) | C(2)-Zr(1)-C(4) | 50.6(2) |
| C(1)-Zr(1)-C(5) | 31.4(2) | N(1)-Zr(1)-C(3) | 90.47(19) |
| C(10)-Zr(1)-C(5) | 98.4(3) | N(1)#1-Zr(1)-C(3) | 130.21(19) |
| N(1)-Zr(1)-C(7) | 104.98(19) | C(6)-Zr(1)-C(3) | 121.3(2) |
| N(1)#1-Zr(1)-C(7) | 85.30(18) | C(1)-Zr(1)-C(3) | 51.4(2) |
| C(6)-Zr(1)-C(7) | 30.9(2) | C(10)-Zr(1)-C(3) | 93.9(2) |
| C(1)-Zr(1)-C(7) | 140.0(2) | C(5)-Zr(1)-C(3) | 51.0(2) |
| C(10)-Zr(1)-C(7) | 50.9(2) | C(7)-Zr(1)-C(3) | 143.6(2) |
| C(5)-Zr(1)-C(7) | 117.2(2) | C(2)-Zr(1)-C(3) | 31.3(2) |
| N(1)-Zr(1)-C(2) | 86.7(2) | C(4)-Zr(1)-C(3) | 30.09(19) |
| N(1)#1-Zr(1)-C(2) | 99.00(19) | N(1)-Zr(1)-C(8) | 134.7(2) |
| C(6)-Zr(1)-C(2) | 151.7(2) | N(1)#1-Zr(1)-C(8) | 95.42(19) |
| C(1)-Zr(1)-C(2) | 30.5(2) | C(6)-Zr(1)-C(8) | 50.8(2) |
| C(10)-Zr(1)-C(2) | 125.0(2) | C(1)-Zr(1)-C(8) | 112.4(2) |
| C(5)-Zr(1)-C(2) | 50.9(2) | C(10)-Zr(1)-C(8) | 50.7(2) |
| C(7)-Zr(1)-C(2) | 168.1(2) | C(5)-Zr(1)-C(8) | 87.1(2) |
| N(1)-Zr(1)-C(4) | 119.20(19) | C(7)-Zr(1)-C(8) | 30.2(2) |
| N(1)#1-Zr(1)-C(4) | 137.57(19) | C(2)-Zr(1)-C(8) | 137.9(2) |
| C(6)-Zr(1)-C(4) | 110.6(2) | C(4)-Zr(1)-C(8) | 93.8(2) |
| C(1)-Zr(1)-C(4) | 51.4(2) | C(3)-Zr(1)-C(8) | 122.9(2) |
| C(10)-Zr(1)-C(4) | 79.3(2) | N(1)-Zr(1)-C(9) | 133.4(2) |
| C(5)-Zr(1)-C(4) | 31.2(2) | N(1)#1-Zr(1)-C(9) | 125.1(2) |

| | | | |
|---|---|---|---|
| C(6)-Zr(1)-C(9) | 50.7(2) | C(1)-C(5)-C(4) | 107.2(6) |
| C(1)-Zr(1)-C(9) | 107.2(2) | C(1)-C(5)-Zr(1) | 73.3(4) |
| C(10)-Zr(1)-C(9) | 30.8(2) | C(4)-C(5)-Zr(1) | 76.0(4) |
| C(5)-Zr(1)-C(9) | 76.1(2) | C(7)-C(6)-C(10) | 107.6(7) |
| C(7)-Zr(1)-C(9) | 49.7(2) | C(7)-C(6)-Zr(1) | 76.2(4) |
| C(2)-Zr(1)-C(9) | 120.2(2) | C(10)-C(6)-Zr(1) | 75.6(4) |
| C(4)-Zr(1)-C(9) | 69.9(2) | C(8)-C(7)-C(6) | 109.5(6) |
| C(3)-Zr(1)-C(9) | 96.0(2) | C(8)-C(7)-Zr(1) | 77.8(4) |
| C(8)-Zr(1)-C(9) | 29.8(2) | C(6)-C(7)-Zr(1) | 72.9(3) |
| C(2)-C(1)-C(5) | 108.2(6) | C(7)-C(8)-C(9) | 107.8(6) |
| C(2)-C(1)-Zr(1) | 76.2(4) | C(7)-C(8)-Zr(1) | 72.0(4) |
| C(5)-C(1)-Zr(1) | 75.3(4) | C(9)-C(8)-Zr(1) | 76.1(4) |
| C(1)-C(2)-C(3) | 108.8(6) | C(8)-C(9)-C(10) | 107.7(7) |
| C(1)-C(2)-Zr(1) | 73.3(4) | C(8)-C(9)-Zr(1) | 74.1(4) |
| C(3)-C(2)-Zr(1) | 75.6(4) | C(10)-C(9)-Zr(1) | 70.4(4) |
| C(4)-C(3)-C(2) | 107.1(6) | C(6)-C(10)-C(9) | 107.4(7) |
| C(4)-C(3)-Zr(1) | 74.9(4) | C(6)-C(10)-Zr(1) | 73.1(4) |
| C(2)-C(3)-Zr(1) | 73.1(3) | C(9)-C(10)-Zr(1) | 78.8(4) |
| C(3)-C(4)-C(5) | 108.6(6) | Sn(1)-N(1)-Zr(1) | 131.0(2) |
| C(3)-C(4)-Zr(1) | 75.0(4) | Sn(1)-N(1)-Zr(1)#1 | 129.1(2) |
| C(5)-C(4)-Zr(1) | 72.8(4) | Zr(1)-N(1)-Zr(1)#1 | 99.05(17) |

**Table A.45**. Anisotropic displacement parameters ($Å^2$ x $10^3$) for $C_{26}H_{38}N_2Sn_2Zr_2$ (**12**).

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Sn(1) | 43(1) | 34(1) | 34(1) | 2(1) | 9(1) | -5(1) |
| Zr(1) | 35(1) | 31(1) | 34(1) | -1(1) | 11(1) | 0(1) |
| C(1) | 50(4) | 50(4) | 80(5) | -24(4) | 26(4) | 1(3) |
| C(2) | 59(4) | 50(4) | 64(5) | -14(3) | 9(4) | 18(3) |
| C(3) | 67(4) | 41(3) | 52(4) | -8(3) | 18(3) | 3(3) |
| C(4) | 63(4) | 56(4) | 42(4) | -13(3) | 8(3) | 3(3) |
| C(5) | 90(5) | 54(4) | 49(4) | 4(3) | 31(4) | 4(4) |
| C(6) | 39(3) | 58(4) | 71(5) | 5(3) | 8(3) | 14(3) |
| C(7) | 50(4) | 44(3) | 53(4) | 2(3) | -2(3) | 6(3) |
| C(8) | 52(4) | 60(4) | 62(5) | 16(3) | 10(3) | 0(3) |
| C(9) | 59(4) | 81(5) | 48(4) | -4(4) | -7(3) | 10(4) |
| C(10) | 41(4) | 53(4) | 94(6) | 0(4) | -6(4) | 2(3) |
| C(11) | 56(4) | 54(4) | 49(4) | 1(3) | 1(3) | -12(3) |
| C(12) | 73(4) | 41(3) | 51(4) | 6(3) | 16(3) | -2(3) |
| C(13) | 58(4) | 46(3) | 38(3) | 0(3) | 19(3) | -9(3) |
| N(1) | 33(2) | 34(2) | 35(2) | 1(2) | 9(2) | -1(2) |

**Table A.46**. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å $^2$ x $10^3$) for $C_{26}H_{38}N_2Sn_2Zr_2$ (**12**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 2291 | 525 | 7161 | 56(18) |
| H(2) | 3123 | 1638 | 5757 | 110(30) |
| H(3) | 5902 | 2178 | 6785 | 90(30) |
| H(4) | 6699 | 1425 | 8884 | 60(20) |
| H(5) | 4476 | 389 | 9136 | 80(20) |
| H(6) | 9042 | -298 | 5674 | 130(40) |
| H(7) | 7432 | -1491 | 6304 | 80(20) |
| H(8) | 6688 | -1237 | 8513 | 90(30) |
| H(9) | 7963 | 100 | 9340 | 220(60) |
| H(10) | 9304 | 729 | 7519 | 270(70) |
| H(11A) | 8859 | 2168 | 5929 | 80(13) |
| H(11B) | 9775 | 2295 | 4720 | 80(13) |
| H(11C) | 9752 | 1424 | 5372 | 80(13) |
| H(12A) | 4479 | 2635 | 3139 | 118(18) |
| H(12B) | 5978 | 3170 | 3756 | 118(18) |
| H(12C) | 4921 | 2703 | 4662 | 118(18) |
| H(13A) | 8522 | 1155 | 1968 | 121(18) |
| H(13B) | 7323 | 1865 | 1419 | 121(18) |
| H(13C) | 6660 | 965 | 1521 | 121(18) |

**Table A.47**. Atomic Coordinates (x $10^4$) and Equivalent Isotropic Displacement Parameters (Å x $10^3$) for $C_{12}H_{36}N_4Si_4Sn_4$ (**13**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Sn(1) | 833(1) | 0 | 702(1) | 36(1) |
| Sn(2) | 122(1) | 370(1) | 552(1) | 40(1) |
| Sn(3) | 1966(1) | 0 | 972(1) | 38(1) |
| Si(1) | 1143(1) | 0 | 0008(2) | 65(1) |
| Si(2) | 3095(1) | 0 | 737(2) | 43(1) |
| Si(3) | 1216(1) | 381(1) | 526(1) | 49(1) |
| N(1) | 1397(2) | 0 | 738(5) | 39(1) |
| N(2) | 2385(2) | 0 | 095(4) | 34(1) |
| N(3) | 1432(1) | 202(3) | 468(3) | 36(1) |
| C(1) | 724(3) | 250(7) | 887(6) | 113(3) |
| C(2) | 1723(4) | 0 | 1583(7) | 94(3) |
| C(3) | 3347(2) | 278(6) | 186(7) | 103(3) |
| C(4) | 3327(3) | 0 | 0531(7) | 64(2) |
| C(5) | 1811(3) | 242(5) | 613(7) | 93(2) |
| C(6) | 755(2) | 197(5) | 155(6) | 76(2) |
| C(7) | 833(2) | 967(5) | 812(4) | 74(2) |
| C(8) | 5000(2) | 38(5) | 0000(4) | 51(4) |
| C(9) | 4934(2) | 0(5) | 036(4) | 48(3) |
| C(10) | 4965(2) | 989(5) | 0950(4) | 78(4) |
| C(11) | 5167(2) | 0(4) | 2492(4) | 113(8) |

| | | | | |
|---|---|---|---|---|
| C(12) | 4983(2) | 0(4) | 11805(4) | 65(4) |
| C(13) | 5118(2) | 1019(5) | 10534(4) | 52(5) |

**Table A.48**. Interatomic Distances (Å) and Angles (°) for $C_{12}H_{36}N_4Si_4Sn_4$ (**13**).

| | | | |
|---|---|---|---|
| Sn(1)-N(1) | 2.205(5) | N(2)-Sn(2)#1 | 2.203(3) |
| Sn(1)-N(3) | 2.208(4) | C(8)-C(13) | 0.5669 |
| Sn(1)-N(3)#1 | 2.208(4) | C(8)-C(13)#2 | 0.567(9) |
| Sn(2)-N(1) | 2.198(4) | C(8)-C(10) | 1.0752 |
| Sn(2)-N(2) | 2.203(3) | C(8)-C(10)#2 | 1.075(10) |
| Sn(2)-N(3) | 2.204(4) | C(8)-C(9)#3 | 1.515(12) |
| Sn(3)-N(2) | 2.198(5) | C(8)-C(9) | 1.5146 |
| Sn(3)-N(3)#1 | 2.204(4) | C(9)-C(12)#3 | 1.015(10) |
| Sn(3)-N(3) | 2.204(4) | C(9)-C(10)#2 | 1.221(2) |
| Si(1)-N(1) | 1.731(5) | C(9)-C(10)#3 | 1.222(10) |
| Si(1)-C(1)#1 | 1.841(7) | C(9)-C(13)#2 | 1.339(4) |
| Si(1)-C(1) | 1.841(7) | C(9)-C(13)#3 | 1.339(12) |
| Si(1)-C(2) | 1.857(8) | C(9)-C(8)#3 | 1.515(11) |
| Si(2)-N(2) | 1.735(5) | C(9)-C(11)#3 | 1.599(10) |
| Si(2)-C(4) | 1.842(7) | C(9)-C(13) | 1.9701 |
| Si(2)-C(3)#1 | 1.857(6) | C(9)-C(13)#1 | 1.970(7) |
| Si(2)-C(3) | 1.857(6) | C(9)-C(9)#3 | 2.014(10) |
| Si(3)-N(3) | 1.732(4) | C(10)-C(13) | 0.7007 |
| Si(3)-C(5) | 1.842(6) | C(10)-C(9)#3 | 1.222(10) |
| Si(3)-C(6) | 1.858(6) | C(10)-C(12) | 1.5068 |
| Si(3)-C(7) | 1.862(5) | C(10)-C(13)#2 | 1.562(10) |
| N(1)-Sn(2)#1 | 2.198(4) | C(10)-C(11) | 1.9829 |

| | | | |
|---|---|---|---|
| C(11)-C(12) | 0.7389 | C(1)#1-Si(1)-C(2) | 109.8(3) |
| C(11)-C(9)#3 | 1.599(10) | C(1)-Si(1)-C(2) | 109.8(3) |
| C(11)-C(10)#1 | 1.983(6) | N(2)-Si(2)-C(4) | 110.1(3) |
| C(12)-C(9)#3 | 1.015(11) | N(2)-Si(2)-C(3)#1 | 108.4(2) |
| C(12)-C(10)#1 | 1.507(8) | C(4)-Si(2)-C(3)#1 | 108.8(3) |
| C(12)-C(13) | 1.9749 | N(2)-Si(2)-C(3) | 108.4(2) |
| C(12)-C(13)#1 | 1.975(6) | C(4)-Si(2)-C(3) | 108.8(3) |
| C(13)-C(13)#2 | 1.117(9) | C(3)#1-Si(2)-C(3) | 112.3(5) |
| C(13)-C(9)#3 | 1.339(12) | N(3)-Si(3)-C(5) | 109.7(2) |
| C(13)-C(10)#2 | 1.562(10) | N(3)-Si(3)-C(6) | 109.5(2) |
| N(1)-Sn(1)-N(3) | 82.28(13) | C(5)-Si(3)-C(6) | 108.8(3) |
| N(1)-Sn(1)-N(3)#1 | 82.28(13) | N(3)-Si(3)-C(7) | 109.2(2) |
| N(3)-Sn(1)-N(3)#1 | 82.08(19) | C(5)-Si(3)-C(7) | 110.6(3) |
| N(1)-Sn(2)-N(2) | 82.19(15) | C(6)-Si(3)-C(7) | 109.0(2) |
| N(1)-Sn(2)-N(3) | 82.51(16) | Si(1)-N(1)-Sn(2) | 119.72(16) |
| N(2)-Sn(2)-N(3) | 82.17(15) | Si(1)-N(1)-Sn(2)#1 | 119.72(16) |
| N(2)-Sn(3)-N(3)#1 | 82.31(13) | Sn(2)-N(1)-Sn(2)#1 | 97.5(2) |
| N(2)-Sn(3)-N(3) | 82.31(13) | Si(1)-N(1)-Sn(1) | 120.3(3) |
| N(3)#1-Sn(3)-N(3) | 82.29(19) | Sn(2)-N(1)-Sn(1) | 97.22(16) |
| N(1)-Si(1)-C(1)#1 | 108.9(3) | Sn(2)#1-N(1)-Sn(1) | 97.22(16) |
| N(1)-Si(1)-C(1) | 108.9(3) | Si(2)-N(2)-Sn(3) | 119.9(3) |
| C(1)#1-Si(1)-C(1) | 110.1(5) | Si(2)-N(2)-Sn(2)#1 | 119.90(15) |
| N(1)-Si(1)-C(2) | 109.3(4) | Sn(3)-N(2)-Sn(2)#1 | 97.36(14) |

| | | | |
|---|---|---|---|
| Si(2)-N(2)-Sn(2) | 119.90(15) | C(9)#3-C(8)-C(9) | 83.3(3) |
| Sn(3)-N(2)-Sn(2) | 97.36(14) | C(12)#3-C(9)-C(10)#2 | 84.2(9) |
| Sn(2)#1-N(2)-Sn(2) | 97.2(2) | C(12)#3-C(9)-C(10)#3 | 84.1(6) |
| Si(3)-N(3)-Sn(3) | 119.86(19) | C(10)#2-C(9)-C(10)#3 | 155.4(9) |
| Si(3)-N(3)-Sn(2) | 119.50(19) | C(12)#3-C(9)-C(13)#2 | 113.4(8) |
| Sn(3)-N(3)-Sn(2) | 97.17(13) | C(10)#2-C(9)-C(13)#2 | 31.34(8) |
| Si(3)-N(3)-Sn(1) | 120.68(18) | C(10)#3-C(9)-C(13)#2 | 160.1(8) |
| Sn(3)-N(3)-Sn(1) | 97.36(15) | C(12)#3-C(9)-C(13)#3 | 113.3(8) |
| Sn(2)-N(3)-Sn(1) | 96.94(14) | C(10)#2-C(9)-C(13)#3 | 160.1(8) |
| C(13)-C(8)-C(13)#2 | 160.14(17) | C(10)#3-C(9)-C(13)#3 | 31.3(3) |
| C(13)-C(8)-C(10) | 36.0 | C(13)#2-C(9)-C(13)#3 | 133.3(8) |
| C(13)#2-C(8)-C(10) | 142.1(10) | C(12)#3-C(9)-C(8)#3 | 128.4(8) |
| C(13)-C(8)-C(10)#2 | 142.1(4) | C(10)#2-C(9)-C(8)#3 | 138.5(7) |
| C(13)#2-C(8)-C(10)#2 | 36.0(7) | C(10)#3-C(9)-C(8)#3 | 44.7(4) |
| C(10)-C(8)-C(10)#2 | 173.37(6) | C(13)#2-C(9)-C(8)#3 | 116.3(7) |
| C(13)-C(8)-C(9)#3 | 61.4(3) | C(13)#3-C(9)-C(8)#3 | 21.81(18) |
| C(13)#2-C(8)-C(9)#3 | 137.5(6) | C(12)#3-C(9)-C(8) | 128.4(6) |
| C(10)-C(8)-C(9)#3 | 53.0(3) | C(10)#2-C(9)-C(8) | 44.7(5) |
| C(10)#2-C(8)-C(9)#3 | 133.4(4) | C(10)#3-C(9)-C(8) | 138.5(4) |
| C(13)-C(8)-C(9) | 137.5 | C(13)#2-C(9)-C(8) | 21.8(4) |
| C(13)#2-C(8)-C(9) | 61.3(4) | C(13)#3-C(9)-C(8) | 116.3(4) |
| C(10)-C(8)-C(9) | 133.4 | C(8)#3-C(9)-C(8) | 96.7(3) |
| C(10)#2-C(8)-C(9) | 53.04(10) | C(12)#3-C(9)-C(11)#3 | 20.5(2) |

| | | | |
|---|---|---|---|
| C(10)#2-C(9)-C(11)#3 | 88.3(7) | C(12)#3-C(9)-C(9)#3 | 159.1(8) |
| C(10)#3-C(9)-C(11)#3 | 88.3(5) | C(10)#2-C(9)-C(9)#3 | 91.6(5) |
| C(13)#2-C(9)-C(11)#3 | 111.5(6) | C(10)#3-C(9)-C(9)#3 | 91.6(6) |
| C(13)#3-C(9)-C(11)#3 | 111.5(6) | C(13)#2-C(9)-C(9)#3 | 68.6(4) |
| C(8)#3-C(9)-C(11)#3 | 131.7(7) | C(13)#3-C(9)-C(9)#3 | 68.6(5) |
| C(8)-C(9)-C(11)#3 | 131.7(4) | C(8)#3-C(9)-C(9)#3 | 48.3(3) |
| C(12)#3-C(9)-C(13) | 133.3(6) | C(8)-C(9)-C(9)#3 | 48.3(3) |
| C(10)#2-C(9)-C(13) | 52.4(5) | C(11)#3-C(9)-C(9)#3 | 179.6(6) |
| C(10)#3-C(9)-C(13) | 127.6(4) | C(13)-C(9)-C(9)#3 | 39.3(3) |
| C(13)#2-C(9)-C(13) | 33.0(4) | C(13)#1-C(9)-C(9)#3 | 39.24(7) |
| C(13)#3-C(9)-C(13) | 107.8(4) | C(13)-C(10)-C(8) | 28.4 |
| C(8)#3-C(9)-C(13) | 87.2(3) | C(13)-C(10)-C(9)#3 | 83.6(6) |
| C(8)-C(9)-C(13) | 11.2 | C(8)-C(10)-C(9)#3 | 82.3(5) |
| C(11)#3-C(9)-C(13) | 140.7(4) | C(13)-C(10)-C(12) | 122.6 |
| C(12)#3-C(9)-C(13)#1 | 133.3(8) | C(8)-C(10)-C(12) | 124.0 |
| C(10)#2-C(9)-C(13)#1 | 127.6(4) | C(9)#3-C(10)-C(12) | 42.1(5) |
| C(10)#3-C(9)-C(13)#1 | 52.4(6) | C(13)-C(10)-C(13)#2 | 39.8(3) |
| C(13)#2-C(9)-C(13)#1 | 107.8(4) | C(8)-C(10)-C(13)#2 | 12.9(3) |
| C(13)#3-C(9)-C(13)#1 | 33.0(4) | C(9)#3-C(10)-C(13)#2 | 89.3(5) |
| C(8)#3-C(9)-C(13)#1 | 11.2(3) | C(12)-C(10)-C(13)#2 | 128.8 |
| C(8)-C(9)-C(13)#1 | 87.2(3) | C(13)-C(10)-C(11) | 122.5 |
| C(11)#3-C(9)-C(13)#1 | 140.7(6) | C(8)-C(10)-C(11) | 134.4 |
| C(13)-C(9)-C(13)#1 | 77.2(3) | C(9)#3-C(10)-C(11) | 53.7(5) |

| | | | |
|---|---|---|---|
| C(12)-C(10)-C(11) | 18.8 | C(8)-C(13)-C(10) | 115.6 |
| C(13)#2-C(10)-C(11) | 142.95(9) | C(8)-C(13)-C(13)#2 | 9.9 |
| C(12)-C(11)-C(9)#3 | 28.7(4) | C(10)-C(13)-C(13)#2 | 116.6(5) |
| C(12)-C(11)-C(10) | 41.1 | C(8)-C(13)-C(9)#3 | 96.8(4) |
| C(9)#3-C(11)-C(10) | 38.0(4) | C(10)-C(13)-C(9)#3 | 65.1(4) |
| C(12)-C(11)-C(10)#1 | 41.1(2) | C(13)#2-C(13)-C(9)#3 | 106.3(4) |
| C(9)#3-C(11)-C(10)#1 | 38.00(19) | C(8)-C(13)-C(10)#2 | 25.0(3) |
| C(10)-C(11)-C(10)#1 | 74.0(3) | C(10)-C(13)-C(10)#2 | 140.0(3) |
| C(11)-C(12)-C(9)#3 | 130.8(5) | C(13)#2-C(13)-C(10)#2 | 23.6(2) |
| C(11)-C(12)-C(10) | 120.1 | C(9)#3-C(13)-C(10)#2 | 110.4(4) |
| C(9)#3-C(12)-C(10) | 53.8(6) | C(8)-C(13)-C(9) | 31.3 |
| C(11)-C(12)-C(10)#1 | 120.06(18) | C(10)-C(13)-C(9) | 118.5 |
| C(9)#3-C(12)-C(10)#1 | 53.7(4) | C(13)#2-C(13)-C(9) | 40.69(16) |
| C(10)-C(12)-C(10)#1 | 104.8(3) | C(9)#3-C(13)-C(9) | 72.2(4) |
| C(11)-C(12)-C(13) | 120.3 | C(10)#2-C(13)-C(9) | 38.31(8) |
| C(9)#3-C(12)-C(13) | 38.5(6) | C(8)-C(13)-C(12) | 117.0 |
| C(10)-C(12)-C(13) | 17.4 | C(10)-C(13)-C(12) | 40.0 |
| C(10)#1-C(12)-C(13) | 91.8(3) | C(13)#2-C(13)-C(12) | 124.7(3) |
| C(11)-C(12)-C(13)#1 | 120.26(12) | C(9)#3-C(13)-C(12) | 28.2(4) |
| C(9)#3-C(12)-C(13)#1 | 38.5(4) | C(10)#2-C(13)-C(12) | 136.24(14) |
| C(10)-C(12)-C(13)#1 | 91.8(3) | C(9)-C(13)-C(12) | 98.3 |
| C(10)#1-C(12)-C(13)#1 | 17.4 | | |
| C(13)-C(12)-C(13)#1 | 77.0(3) | | |

**Table A.49**. Anisotropic displacement parameters ($Å^2$ x $10^3$) for $C_{12}H_{36}N_4Si_4Sn_4$ (**13**).

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Sn(1) | 26(1) | 44(1) | 33(1) | 0 | 5(1) | 0 |
| Sn(2) | 34(1) | 41(1) | 38(1) | -8(1) | 3(1) | 0(1) |
| Sn(3) | 32(1) | 49(1) | 31(1) | 0 | 10(1) | 0 |
| Si(1) | 39(1) | 123(2) | 35(1) | 0 | 15(1) | 0 |
| Si(2) | 26(1) | 56(1) | 41(1) | 0 | 3(1) | 0 |
| Si(3) | 45(1) | 40(1) | 52(1) | 12(1) | 3(1) | 2(1) |
| N(1) | 33(3) | 50(3) | 32(3) | 0 | 10(2) | 0 |
| N(2) | 25(3) | 42(3) | 33(3) | 0 | 6(2) | 0 |
| N(3) | 34(2) | 35(2) | 35(2) | 4(2) | 6(2) | -1(2) |
| C(1) | 76(5) | 193(9) | 79(5) | -42(5) | 36(4) | 32(5) |
| C(2) | 91(7) | 154(10) | 36(5) | 0 | 19(5) | 0 |
| C(3) | 47(4) | 144(7) | 101(5) | 49(5) | 4(3) | -33(4) |
| C(4) | 46(4) | 84(6) | 44(4) | 0 | -8(3) | 0 |
| C(5) | 80(5) | 65(4) | 121(6) | 43(4) | 17(4) | -13(4) |
| C(6) | 73(4) | 55(4) | 79(4) | -8(3) | -1(3) | 19(3) |
| C(7) | 76(4) | 82(4) | 51(4) | 22(3) | 5(3) | 14(3) |

**Table A.50**. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å $^2$ x $10^3$) for $C_{12}H_{36}N_4Si_4Sn_4$ (**13**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 929 | 1887 | 9832 | 94(13) |
| H(1B) | 620 | 1305 | 10637 | 94(13) |
| H(1C) | 405 | 1205 | 9130 | 94(13) |
| H(2A) | 1893 | -708 | 11722 | 70(20) |
| H(2B) | 1591 | 161 | 12271 | 70(20) |
| H(2C) | 1982 | 547 | 11560 | 70(20) |
| H(3A) | 3219 | 1299 | 7261 | 160(20) |
| H(3B) | 3736 | 1281 | 8509 | 160(20) |
| H(3C) | 3216 | 1910 | 8507 | 160(20) |
| H(4A) | 3258 | 705 | 10829 | 90(20) |
| H(4B) | 3708 | -152 | 10872 | 90(20) |
| H(4C) | 3135 | -553 | 10817 | 90(20) |
| H(5A) | 1983 | 3497 | 6480 | 115(15) |
| H(5B) | 1693 | 3859 | 5045 | 115(15) |
| H(5C) | 2063 | 2814 | 5357 | 115(15) |
| H(6A) | 443 | 2765 | 6102 | 104(13) |
| H(6B) | 642 | 3850 | 5648 | 104(13) |
| H(6C) | 944 | 3394 | 7038 | 104(13) |
| H(7A) | 1080 | 1652 | 3439 | 124(15) |
| H(7B) | 664 | 2601 | 3324 | 124(15) |
| H(7C) | 562 | 1437 | 3798 | 124(15) |

**Table A.51**. Atomic Coordinates (x $10^4$) and Equivalent Isotropic Displacement Parameters (Å x $10^3$) for $C_{12}H_{36}N_4Ge_4Si_4$ (**14**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Ge(1) | 1946(1) | 5100(1) | 3065(1) | 30(1) |
| Ge(2) | 1926(1) | 3699(1) | 4206(1) | 31(1) |
| Ge(3) | 1895(1) | 6203(1) | 4291(1) | 30(1) |
| Ge(4) | 911(1) | 4962(1) | 3389(1) | 32(1) |
| Si(1) | 3077(1) | 5077(1) | 4379(1) | 33(1) |
| Si(2) | 1210(1) | 7391(1) | 2859(1) | 37(1) |
| Si(3) | 1161(1) | 4756(1) | 4990(1) | 38(1) |
| Si(4) | 1245(1) | 2742(1) | 2711(1) | 40(1) |
| N(1) | 2355(1) | 5022(2) | 4053(2) | 29(1) |
| N(2) | 1442(1) | 6157(2) | 3316(1) | 30(1) |
| N(3) | 1419(1) | 4890(2) | 4344(2) | 30(1) |
| N(4) | 1464(1) | 3894(2) | 3236(1) | 32(1) |
| C(1) | 3294(2) | 6506(4) | 4219(2) | 55(1) |
| C(2) | 3361(2) | 3994(4) | 3967(2) | 62(1) |
| C(3) | 3322(2) | 4818(4) | 5286(2) | 56(1) |
| C(4) | 1817(2) | 8316(4) | 2964(3) | 65(1) |
| C(5) | 730(2) | 8118(4) | 3200(2) | 53(1) |
| C(6) | 852(2) | 7017(4) | 1968(2) | 61(1) |
| C(7) | 1749(2) | 4774(4) | 5791(2) | 61(1) |
| C(8) | 677(2) | 5939(4) | 4945(2) | 57(1) |

| | | | | |
|---|---|---|---|---|
| C(9) | 776(2) | 3400(4) | 4875(2) | 55(1) |
| C(10) | 1859(2) | 1928(4) | 2721(3) | 74(2) |
| C(11) | 851(2) | 3271(4) | 1860(2) | 65(1) |
| C(12) | 792(2) | 1845(4) | 3015(2) | 64(1) |
| C(13) | 4913(4) | 5128(7) | 4472(5) | 42(2) |
| C(13A) | 4832(5) | 5224(9) | 3737(7) | 74(3) |
| C(14) | 4857(3) | 6088(7) | 4806(5) | 37(2) |
| C(14A) | 4922(5) | 5969(13) | 4502(8) | 89(4) |
| C(15) | 4907(4) | 5992(8) | 5496(5) | 54(2) |
| C(15A) | 4956(4) | 5938(9) | 5150(6) | 55(2) |
| C(16) | 4981(6) | 5001(9) | 4147(8) | 74(3) |

**Table A.52**. Interatomic Distances (Å) and Angles (°) for $C_{12}H_{36}N_4Ge_4Si_4$ (**14**).

| | | | |
|---|---|---|---|
| Ge(1)-N(1) | 2.010(3) | Si(3)-C(8) | 1.858(4) |
| Ge(1)-N(2) | 2.013(3) | Si(3)-C(9) | 1.862(4) |
| Ge(1)-N(4) | 2.013(3) | Si(4)-N(4) | 1.735(3) |
| Ge(2)-N(1) | 2.014(3) | Si(4)-C(10) | 1.849(5) |
| Ge(2)-N(4) | 2.015(3) | Si(4)-C(11) | 1.859(5) |
| Ge(2)-N(3) | 2.016(3) | Si(4)-C(12) | 1.861(4) |
| Ge(3)-N(2) | 2.006(3) | C(13)-C(16) | 0.792(15) |
| Ge(3)-N(3) | 2.012(3) | C(13)-C(14A) | 1.000(14) |
| Ge(3)-N(1) | 2.015(3) | C(13)-C(14) | 1.382(12) |
| Ge(4)-N(3) | 2.007(3) | C(13)-C(15)#1 | 1.403(13) |
| Ge(4)-N(2) | 2.013(3) | C(13)-C(15A)#1 | 1.478(13) |
| Ge(4)-N(4) | 2.018(3) | C(13)-C(13A) | 1.521(16) |
| Si(1)-N(1) | 1.740(3) | C(13)-C(15A) | 1.717(14) |
| Si(1)-C(3) | 1.848(5) | C(13A)-C(16) | 0.868(17) |
| Si(1)-C(2) | 1.853(4) | C(13A)-C(14A) | 1.81(2) |
| Si(1)-C(1) | 1.856(4) | C(14)-C(15A) | 0.713(12) |
| Si(2)-N(2) | 1.748(3) | C(14)-C(14A) | 0.743(14) |
| Si(2)-C(4) | 1.857(5) | C(14)-C(15) | 1.445(13) |
| Si(2)-C(5) | 1.858(4) | C(14)-C(16) | 2.024(16) |
| Si(2)-C(6) | 1.861(4) | C(14A)-C(15A) | 1.364(17) |
| Si(3)-N(3) | 1.745(3) | C(14A)-C(16) | 1.417(19) |
| Si(3)-C(7) | 1.847(5) | C(15)-C(15A) | 0.798(12) |

| | | | |
|---|---|---|---|
| C(15)-C(16)#1 | 1.381(15) | C(2)-Si(1)-C(1) | 110.6(2) |
| C(15)-C(13)#1 | 1.403(13) | N(2)-Si(2)-C(4) | 108.86(18) |
| C(15A)-C(13)#1 | 1.478(13) | N(2)-Si(2)-C(5) | 108.07(18) |
| C(15A)-C(16)#1 | 1.838(19) | C(4)-Si(2)-C(5) | 109.0(2) |
| C(16)-C(15)#1 | 1.381(15) | N(2)-Si(2)-C(6) | 108.93(19) |
| C(16)-C(15A)#1 | 1.838(19) | C(4)-Si(2)-C(6) | 110.8(2) |
| N(1)-Ge(1)-N(2) | 83.84(12) | C(5)-Si(2)-C(6) | 111.1(2) |
| N(1)-Ge(1)-N(4) | 84.36(11) | N(3)-Si(3)-C(7) | 108.8(2) |
| N(2)-Ge(1)-N(4) | 84.07(13) | N(3)-Si(3)-C(8) | 109.04(18) |
| N(1)-Ge(2)-N(4) | 84.22(12) | C(7)-Si(3)-C(8) | 110.8(2) |
| N(1)-Ge(2)-N(3) | 84.13(11) | N(3)-Si(3)-C(9) | 107.93(18) |
| N(4)-Ge(2)-N(3) | 83.96(13) | C(7)-Si(3)-C(9) | 110.9(2) |
| N(2)-Ge(3)-N(3) | 83.99(13) | C(8)-Si(3)-C(9) | 109.4(2) |
| N(2)-Ge(3)-N(1) | 83.90(12) | N(4)-Si(4)-C(10) | 108.94(19) |
| N(3)-Ge(3)-N(1) | 84.22(11) | N(4)-Si(4)-C(11) | 108.17(19) |
| N(3)-Ge(4)-N(2) | 83.95(11) | C(10)-Si(4)-C(11) | 110.8(3) |
| N(3)-Ge(4)-N(4) | 84.12(11) | N(4)-Si(4)-C(12) | 108.86(19) |
| N(2)-Ge(4)-N(4) | 83.96(13) | C(10)-Si(4)-C(12) | 109.7(2) |
| N(1)-Si(1)-C(3) | 109.7(2) | C(11)-Si(4)-C(12) | 110.3(2) |
| N(1)-Si(1)-C(2) | 109.09(17) | Si(1)-N(1)-Ge(1) | 120.64(17) |
| C(3)-Si(1)-C(2) | 110.0(2) | Si(1)-N(1)-Ge(2) | 122.22(15) |
| N(1)-Si(1)-C(1) | 107.91(16) | Ge(1)-N(1)-Ge(2) | 95.46(12) |
| C(3)-Si(1)-C(1) | 109.6(2) | Si(1)-N(1)-Ge(3) | 120.76(15) |

| | | | |
|---|---|---|---|
| Ge(1)-N(1)-Ge(3) | 95.78(13) | C(16)-C(13)-C(15)#1 | 71.9(12) |
| Ge(2)-N(1)-Ge(3) | 95.52(13) | C(14A)-C(13)-C(15)#1 | 160.7(13) |
| Si(2)-N(2)-Ge(3) | 121.38(16) | C(14)-C(13)-C(15)#1 | 148.2(10) |
| Si(2)-N(2)-Ge(4) | 121.94(15) | C(16)-C(13)-C(15A)#1 | 103.9(14) |
| Ge(3)-N(2)-Ge(4) | 95.72(12) | C(14A)-C(13)-C(15A)#1 | 145.5(14) |
| Si(2)-N(2)-Ge(1) | 119.78(15) | C(14)-C(13)-C(15A)#1 | 117.9(9) |
| Ge(3)-N(2)-Ge(1) | 95.94(12) | C(15)#1-C(13)-C(15A)#1 | 32.0(5) |
| Ge(4)-N(2)-Ge(1) | 95.76(12) | C(16)-C(13)-C(13A) | 24.8(12) |
| Si(3)-N(3)-Ge(4) | 121.59(17) | C(14A)-C(13)-C(13A) | 89.1(12) |
| Si(3)-N(3)-Ge(3) | 121.75(16) | C(14)-C(13)-C(13A) | 118.4(8) |
| Ge(4)-N(3)-Ge(3) | 95.71(13) | C(15)#1-C(13)-C(13A) | 92.5(8) |
| Si(3)-N(3)-Ge(2) | 120.05(16) | C(15A)#1-C(13)-C(13A) | 123.7(9) |
| Ge(4)-N(3)-Ge(2) | 95.83(13) | C(16)-C(13)-C(15A) | 152.5(15) |
| Ge(3)-N(3)-Ge(2) | 95.52(13) | C(14A)-C(13)-C(15A) | 52.6(10) |
| Si(4)-N(4)-Ge(1) | 121.49(16) | C(14)-C(13)-C(15A) | 23.6(5) |
| Si(4)-N(4)-Ge(2) | 121.30(16) | C(15)#1-C(13)-C(15A) | 124.6(8) |
| Ge(1)-N(4)-Ge(2) | 95.35(11) | C(15A)#1-C(13)-C(15A) | 94.6(7) |
| Si(4)-N(4)-Ge(4) | 121.01(15) | C(13A)-C(13)-C(15A) | 141.5(8) |
| Ge(1)-N(4)-Ge(4) | 95.61(12) | C(16)-C(13A)-C(13) | 22.5(11) |
| Ge(2)-N(4)-Ge(4) | 95.55(12) | C(16)-C(13A)-C(14A) | 50.2(12) |
| C(16)-C(13)-C(14A) | 103.9(16) | C(13)-C(13A)-C(14A) | 33.6(5) |
| C(16)-C(13)-C(14) | 135.4(14) | C(15A)-C(14)-C(14A) | 139(2) |
| C(14A)-C(13)-C(14) | 31.5(9) | C(15A)-C(14)-C(13) | 105.5(13) |

| | | | |
|---|---|---|---|
| C(14A)-C(14)-C(13) | 44.6(14) | C(13)#1-C(15)-C(14) | 92.0(8) |
| C(15A)-C(14)-C(15) | 18.0(11) | C(14)-C(15A)-C(15) | 146(2) |
| C(14A)-C(14)-C(15) | 156.9(17) | C(14)-C(15A)-C(14A) | 20.9(11) |
| C(13)-C(14)-C(15) | 118.6(8) | C(15)-C(15A)-C(14A) | 166.6(16) |
| C(15A)-C(14)-C(16) | 118.6(13) | C(14)-C(15A)-C(13)#1 | 135.3(15) |
| C(14A)-C(14)-C(16) | 28.6(15) | C(15)-C(15A)-C(13)#1 | 68.8(12) |
| C(13)-C(14)-C(16) | 16.0(6) | C(14A)-C(15A)-C(13)#1 | 120.2(10) |
| C(15)-C(14)-C(16) | 133.4(8) | C(14)-C(15A)-C(13) | 50.9(11) |
| C(14)-C(14A)-C(13) | 104(2) | C(15)-C(15A)-C(13) | 148.2(14) |
| C(14)-C(14A)-C(15A) | 20.1(11) | C(14A)-C(15A)-C(13) | 35.6(7) |
| C(13)-C(14A)-C(15A) | 91.8(13) | C(13)#1-C(15A)-C(13) | 85.4(7) |
| C(14)-C(14A)-C(16) | 137(2) | C(14)-C(15A)-C(16)#1 | 153.9(15) |
| C(13)-C(14A)-C(16) | 32.9(9) | C(15)-C(15A)-C(16)#1 | 44.1(11) |
| C(15A)-C(14A)-C(16) | 123.2(14) | C(14A)-C(15A)-C(16)#1 | 144.1(10) |
| C(14)-C(14A)-C(13A) | 153.8(19) | C(13)#1-C(15A)-C(16)#1 | 24.7(5) |
| C(13)-C(14A)-C(13A) | 57.3(11) | C(13)-C(15A)-C(16)#1 | 108.5(8) |
| C(15A)-C(14A)-C(13A) | 148.9(12) | C(13)-C(16)-C(13A) | 133(2) |
| C(16)-C(14A)-C(13A) | 28.0(7) | C(13)-C(16)-C(15)#1 | 75.0(14) |
| C(15A)-C(15)-C(16)#1 | 112.2(15) | C(13A)-C(16)-C(15)#1 | 139.1(18) |
| C(15A)-C(15)-C(13)#1 | 79.2(13) | C(13)-C(16)-C(14A) | 43.2(10) |
| C(16)#1-C(15)-C(13)#1 | 33.1(6) | C(13A)-C(16)-C(14A) | 101.8(16) |
| C(15A)-C(15)-C(14) | 16.1(10) | C(15)#1-C(16)-C(14A) | 115.8(15) |
| C(16)#1-C(15)-C(14) | 124.3(11) | C(13)-C(16)-C(15A)#1 | 51.3(11) |

| | | | |
|---|---|---|---|
| C(13A)-C(16)-C(15A)#1 | 153.9(17) | C(13A)-C(16)-C(14) | 113.1(14) |
| C(15)#1-C(16)-C(15A)#1 | 23.7(6) | C(15)#1-C(16)-C(14) | 102.1(10) |
| C(14A)-C(16)-C(15A)#1 | 92.6(12) | C(14A)-C(16)-C(14) | 14.6(7) |
| C(13)-C(16)-C(14) | 28.7(10) | C(15A)#1-C(16)-C(14) | 78.6(7) |

**Table A.53**. Anisotropic displacement parameters ($Å^2$ x $10^3$) for $C_{12}H_{36}N_4Ge_4Si_4$ (**14**).

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Ge(1) | 29(1) | 35(1) | 28(1) | -1(1) | 12(1) | -1(1) |
| Ge(2) | 28(1) | 32(1) | 29(1) | 2(1) | 6(1) | -4(1) |
| Ge(3) | 27(1) | 33(1) | 31(1) | -5(1) | 12(1) | -5(1) |
| Ge(4) | 23(1) | 40(1) | 30(1) | 0(1) | 7(1) | -4(1) |
| Si(1) | 22(1) | 40(1) | 35(1) | -3(1) | 8(1) | -3(1) |
| Si(2) | 38(1) | 35(1) | 41(1) | 7(1) | 17(1) | 6(1) |
| Si(3) | 32(1) | 53(1) | 33(1) | 0(1) | 16(1) | -9(1) |
| Si(4) | 45(1) | 35(1) | 33(1) | -7(1) | 5(1) | -8(1) |
| N(1) | 26(2) | 30(2) | 31(2) | -4(1) | 10(1) | -3(1) |
| N(2) | 26(1) | 32(2) | 33(2) | -1(1) | 12(1) | -1(1) |
| N(3) | 26(2) | 33(2) | 32(2) | -2(1) | 11(1) | -5(1) |
| N(4) | 27(1) | 33(2) | 33(2) | -3(1) | 8(1) | -5(1) |
| C(1) | 37(2) | 57(3) | 72(3) | 2(2) | 21(2) | -14(2) |
| C(2) | 41(2) | 73(3) | 67(3) | -19(3) | 12(2) | 14(2) |
| C(3) | 40(2) | 77(3) | 41(2) | -1(2) | 3(2) | -8(2) |
| C(4) | 66(3) | 53(3) | 82(4) | 22(3) | 34(3) | -7(2) |
| C(5) | 47(2) | 52(3) | 60(3) | -8(2) | 18(2) | 6(2) |
| C(6) | 66(3) | 75(3) | 37(2) | 16(2) | 12(2) | 25(2) |
| C(7) | 54(3) | 95(4) | 32(2) | 5(2) | 13(2) | -12(2) |
| C(8) | 49(2) | 67(3) | 60(3) | -10(2) | 25(2) | -1(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(9) | 50(2) | 60(3) | 59(3) | 13(2) | 25(2) | -10(2) |
| C(10) | 76(4) | 57(3) | 89(4) | -28(3) | 28(3) | 10(3) |
| C(11) | 84(3) | 64(3) | 32(2) | -5(2) | 2(2) | -18(3) |
| C(12) | 64(3) | 57(3) | 56(3) | 6(2) | 1(2) | -27(2) |

**Table A.54**. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å $^2$ x $10^3$) for $C_{12}H_{36}N_4Ge_4Si_4$ (**14**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 3150 | 6654 | 3755 | 102(12) |
| H(1B) | 3687 | 6546 | 4375 | 102(12) |
| H(1C) | 3154 | 7048 | 4445 | 102(12) |
| H(2A) | 3253 | 3268 | 4061 | 70(8) |
| H(2B) | 3754 | 4044 | 4127 | 70(8) |
| H(2C) | 3221 | 4115 | 3499 | 70(8) |
| H(3A) | 3176 | 5378 | 5493 | 88(11) |
| H(3B) | 3716 | 4846 | 5462 | 88(11) |
| H(3C) | 3200 | 4096 | 5368 | 88(11) |
| H(4A) | 2032 | 8386 | 3424 | 76(9) |
| H(4B) | 1691 | 9039 | 2784 | 76(9) |
| H(4C) | 2039 | 7997 | 2737 | 76(9) |
| H(5A) | 431 | 7630 | 3175 | 75(9) |
| H(5B) | 589 | 8779 | 2949 | 75(9) |
| H(5C) | 924 | 8315 | 3652 | 75(9) |
| H(6A) | 1113 | 6704 | 1796 | 114(13) |
| H(6B) | 692 | 7675 | 1724 | 114(13) |
| H(6C) | 568 | 6483 | 1931 | 114(13) |
| H(7A) | 2003 | 4193 | 5793 | 71(9) |
| H(7B) | 1615 | 4655 | 6145 | 71(9) |
| H(7C) | 1931 | 5482 | 5846 | 71(9) |

| | | | | |
|---|---|---|---|---|
| H(8A) | 864 | 6634 | 4963 | 83(10) |
| H(8B) | 550 | 5893 | 5309 | 83(10) |
| H(8C) | 369 | 5895 | 4539 | 83(10) |
| H(9A) | 468 | 3419 | 4469 | 71(9) |
| H(9B) | 648 | 3289 | 5235 | 71(9) |
| H(9C) | 1016 | 2799 | 4863 | 71(9) |
| H(10A) | 2100 | 2400 | 2590 | 155(17) |
| H(10B) | 1744 | 1313 | 2420 | 155(17) |
| H(10C) | 2050 | 1651 | 3157 | 155(17) |
| H(11A) | 556 | 3739 | 1873 | 106(12) |
| H(11B) | 704 | 2652 | 1571 | 106(12) |
| H(11C) | 1092 | 3693 | 1701 | 106(12) |
| H(12A) | 1008 | 1509 | 3427 | 128(15) |
| H(12B) | 627 | 1273 | 2698 | 128(15) |
| H(12C) | 509 | 2295 | 3077 | 128(15) |

**Table A.55**. Atomic Coordinates (x $10^4$) and Equivalent Isotropic Displacement Parameters (Å x $10^3$) for $C_{12}H_{36}N_4Pb_4Si_4$ (**15**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Pb(1) | 6905(1) | 1604(1) | 693(1) | 22(1) |
| Pb(2) | 6667 | 3333 | 1284(1) | 21(1) |
| Si(1) | 6667 | 3333 | 98(1) | 29(1) |
| Si(2) | 9972(2) | 3757(3) | 1092(1) | 22(1) |
| N(1) | 6667 | 3333 | 451(3) | 20(2) |
| N(2) | 8372(9) | 3535(8) | 970(1) | 20(2) |
| C(1) | 4880(13) | 1903(14) | -42(2) | 47(3) |
| C(2) | 9657(13) | 2116(12) | 1286(3) | 41(2) |
| C(3) | 10784(11) | 5289(11) | 1347(2) | 33(2) |
| C(4) | 11249(11) | 4115(12) | 797(2) | 40(2) |

**Table A.56**. Interatomic Distances (Å) and Angles (°) for $C_{12}H_{36}N_4Pb_4Si_4$ (**15**).

| | | | |
|---|---|---|---|
| Pb(1)-N(2) | 2.298(7) | N(2)-Pb(1)-N(2)#1 | 81.4(4) |
| Pb(1)-N(2)#1 | 2.305(7) | N(2)-Pb(1)-N(1) | 82.3(3) |
| Pb(1)-N(1) | 2.312(6) | N(2)#1-Pb(1)-N(1) | 82.1(3) |
| Pb(1)-Pb(1)#2 | 3.4621(6) | N(2)-Pb(1)-Pb(1)#2 | 41.31(17) |
| Pb(1)-Pb(1)#1 | 3.4621(6) | N(2)#1-Pb(1)-Pb(1)#2 | 84.2(2) |
| Pb(1)-Pb(2) | 3.4693(7) | N(1)-Pb(1)-Pb(1)#2 | 41.52(17) |
| Pb(2)-N(2)#1 | 2.298(7) | N(2)-Pb(1)-Pb(1)#1 | 84.3(2) |
| Pb(2)-N(2) | 2.298(7) | N(2)#1-Pb(1)-Pb(1)#1 | 41.16(18) |
| Pb(2)-N(2)#2 | 2.298(7) | N(1)-Pb(1)-Pb(1)#1 | 41.52(17) |
| Pb(2)-Pb(1)#1 | 3.4693(7) | Pb(1)#2-Pb(1)-Pb(1)#1 | 60.0 |
| Pb(2)-Pb(1)#2 | 3.4693(7) | N(2)-Pb(1)-Pb(2) | 40.98(19) |
| Si(1)-N(1) | 1.693(13) | N(2)#1-Pb(1)-Pb(2) | 41.01(19) |
| Si(1)-C(1)#2 | 1.883(12) | N(1)-Pb(1)-Pb(2) | 85.0(3) |
| Si(1)-C(1) | 1.883(12) | Pb(1)#2-Pb(1)-Pb(2) | 60.069(7) |
| Si(1)-C(1)#1 | 1.883(12) | Pb(1)#1-Pb(1)-Pb(2) | 60.069(7) |
| Si(2)-N(2) | 1.716(9) | N(2)#1-Pb(2)-N(2) | 81.6(3) |
| Si(2)-C(2) | 1.869(10) | N(2)#1-Pb(2)-N(2)#2 | 81.6(3) |
| Si(2)-C(4) | 1.872(10) | N(2)-Pb(2)-N(2)#2 | 81.6(3) |
| Si(2)-C(3) | 1.877(10) | N(2)#1-Pb(2)-Pb(1)#1 | 41.00(19) |
| N(1)-Pb(1)#2 | 2.312(6) | N(2)-Pb(2)-Pb(1)#1 | 84.16(19) |
| N(1)-Pb(1)#1 | 2.312(6) | N(2)#2-Pb(2)-Pb(1)#1 | 41.17(18) |
| N(2)-Pb(1)#2 | 2.305(7) | N(2)#1-Pb(2)-Pb(1) | 41.17(18) |

| | | | |
|---|---|---|---|
| N(2)-Pb(2)-Pb(1) | 41.00(19) | C(2)-Si(2)-C(4) | 109.7(5) |
| N(2)#2-Pb(2)-Pb(1) | 84.16(19) | N(2)-Si(2)-C(3) | 109.7(4) |
| Pb(1)#1-Pb(2)-Pb(1) | 59.862(15) | C(2)-Si(2)-C(3) | 106.8(5) |
| N(2)#1-Pb(2)-Pb(1)#2 | 84.16(19) | C(4)-Si(2)-C(3) | 109.9(5) |
| N(2)-Pb(2)-Pb(1)#2 | 41.17(18) | Si(1)-N(1)-Pb(1) | 120.2(3) |
| N(2)#2-Pb(2)-Pb(1)#2 | 41.00(19) | Si(1)-N(1)-Pb(1)#2 | 120.2(3) |
| Pb(1)#1-Pb(2)-Pb(1)#2 | 59.862(15) | Pb(1)-N(1)-Pb(1)#2 | 97.0(3) |
| Pb(1)-Pb(2)-Pb(1)#2 | 59.862(15) | Si(1)-N(1)-Pb(1)#1 | 120.2(3) |
| N(1)-Si(1)-C(1)#2 | 110.8(4) | Pb(1)-N(1)-Pb(1)#1 | 97.0(3) |
| N(1)-Si(1)-C(1) | 110.8(4) | Pb(1)#2-N(1)-Pb(1)#1 | 97.0(3) |
| C(1)#2-Si(1)-C(1) | 108.1(4) | Si(2)-N(2)-Pb(2) | 119.1(3) |
| N(1)-Si(1)-C(1)#1 | 110.8(4) | Si(2)-N(2)-Pb(1) | 120.6(4) |
| C(1)#2-Si(1)-C(1)#1 | 108.1(4) | Pb(2)-N(2)-Pb(1) | 98.0(3) |
| C(1)-Si(1)-C(1)#1 | 108.1(4) | Si(2)-N(2)-Pb(1)#2 | 118.9(4) |
| N(2)-Si(2)-C(2) | 110.0(4) | Pb(2)-N(2)-Pb(1)#2 | 97.8(3) |
| N(2)-Si(2)-C(4) | 110.6(4) | Pb(1)-N(2)-Pb(1)#2 | 97.5(3) |

**Table A.57**. Anisotropic displacement parameters ($Å^2$ x $10^3$) for $C_{12}H_{36}N_4Pb_4Si_4$ (**15**).

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Pb(1) | 26(1) | 22(1) | 20(1) | -2(1) | 0(1) | 13(1) |
| Pb(2) | 24(1) | 24(1) | 14(1) | 0 | 0 | 12(1) |
| Si(1) | 35(2) | 35(2) | 16(2) | 0 | 0 | 17(1) |
| Si(2) | 21(1) | 28(1) | 19(1) | 0(1) | -2(1) | 14(1) |
| N(1) | 26(4) | 26(4) | 8(5) | 0 | 0 | 13(2) |
| N(2) | 25(4) | 25(4) | 13(4) | 0(2) | 2(2) | 15(3) |
| C(1) | 53(7) | 62(8) | 23(5) | -13(5) | -10(5) | 27(6) |
| C(2) | 47(6) | 31(5) | 52(7) | 9(5) | 0(5) | 24(5) |
| C(3) | 31(5) | 32(5) | 31(5) | -7(4) | -7(4) | 13(4) |
| C(4) | 31(5) | 47(6) | 35(6) | 13(5) | 14(4) | 16(5) |

**Table A.58**. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å $^2$ x $10^3$) for $C_{12}H_{36}N_4Pb_4Si_4$ (**15**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 4653 | 998 | 35 | 50(20) |
| H(1B) | 4929 | 1865 | -240 | 50(20) |
| H(1C) | 4157 | 2123 | 8 | 50(20) |
| H(2A) | 8980 | 1918 | 1431 | 41(18) |
| H(2B) | 10536 | 2273 | 1364 | 41(18) |
| H(2C) | 9292 | 1322 | 1161 | 41(18) |
| H(3A) | 10716 | 6076 | 1274 | 50(20) |
| H(3B) | 11766 | 5575 | 1376 | 50(20) |
| H(3C) | 10281 | 4991 | 1519 | 50(20) |
| H(4A) | 11288 | 3269 | 757 | 260(100) |
| H(4B) | 12180 | 4866 | 847 | 260(100) |
| H(4C) | 10929 | 4391 | 636 | 260(100) |

**Table A.59**. Atomic Coordinates (x $10^4$) and Equivalent Isotropic Displacement Parameters (Å x $10^3$) for $C_{12}H_{36}N_4Sn_4Ge_4$ (**16**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Sn(1) | 8611(1) | 1497(1) | 2195(1) | 39(1) |
| Sn(2) | 9964(1) | 197(1) | 1433(1) | 39(1) |
| Ge(1) | 10071(1) | 2048(1) | 4385(1) | 41(1) |
| Ge(2) | 7539(1) | -356(1) | 1937(1) | 44(1) |
| N(1) | 8766(9) | 289(6) | 2216(8) | 37(3) |
| N(2) | 10042(10) | 1431(6) | 3425(8) | 40(3) |
| C(1) | 8632(15) | 1842(13) | 4688(12) | 68(5) |
| C(2) | 11395(13) | 1758(10) | 5371(10) | 54(4) |
| C(3) | 10242(17) | 3073(9) | 3973(13) | 69(5) |
| C(4) | 8227(19) | -1393(8) | 2039(11) | 66(6) |
| C(5) | 6826(17) | -225(13) | 2829(14) | 80(6) |
| C(6) | 6644(18) | -115(13) | 747(15) | 91(8) |
| O(1) | 5226(9) | 1520(6) | 3453(8) | 69(4) |

**Table A.60**. Interatomic Distances (Å) and Angles (°) for $C_{12}H_{36}N_4Sn_4Ge_4$ (**16**).

| | | | |
|---|---|---|---|
| Sn(1)-N(1) | 2.169(11) | N(2)#1-Sn(2)-N(1)#1 | 81.6(4) |
| Sn(1)-N(2)#1 | 2.187(12) | N(2)-Ge(1)-C(2) | 106.5(7) |
| Sn(1)-N(2) | 2.201(12) | N(2)-Ge(1)-C(3) | 105.4(7) |
| Sn(2)-N(1) | 2.210(11) | C(2)-Ge(1)-C(3) | 110.6(8) |
| Sn(2)-N(2)#1 | 2.219(11) | N(2)-Ge(1)-C(1) | 106.2(7) |
| Sn(2)-N(1)#1 | 2.235(11) | C(2)-Ge(1)-C(1) | 111.5(7) |
| Ge(1)-N(2) | 1.855(12) | C(3)-Ge(1)-C(1) | 115.8(8) |
| Ge(1)-C(2) | 1.964(15) | N(1)-Ge(2)-C(5) | 106.9(8) |
| Ge(1)-C(3) | 1.977(17) | N(1)-Ge(2)-C(6) | 106.8(8) |
| Ge(1)-C(1) | 2.030(18) | C(5)-Ge(2)-C(6) | 115.1(11) |
| Ge(2)-N(1) | 1.865(12) | N(1)-Ge(2)-C(4) | 104.3(7) |
| Ge(2)-C(5) | 1.885(19) | C(5)-Ge(2)-C(4) | 109.8(8) |
| Ge(2)-C(6) | 1.91(2) | C(6)-Ge(2)-C(4) | 113.1(9) |
| Ge(2)-C(4) | 2.032(18) | Ge(2)-N(1)-Sn(1) | 123.3(5) |
| N(1)-Sn(2)#1 | 2.235(11) | Ge(2)-N(1)-Sn(2) | 118.2(6) |
| N(2)-Sn(1)#1 | 2.187(12) | Sn(1)-N(1)-Sn(2) | 98.0(5) |
| N(2)-Sn(2)#1 | 2.219(11) | Ge(2)-N(1)-Sn(2)#1 | 118.5(6) |
| N(1)-Sn(1)-N(2)#1 | 82.8(4) | Sn(1)-N(1)-Sn(2)#1 | 97.1(4) |
| N(1)-Sn(1)-N(2) | 83.5(4) | Sn(2)-N(1)-Sn(2)#1 | 96.3(4) |
| N(2)#1-Sn(1)-N(2) | 81.5(5) | Ge(1)-N(2)-Sn(1)#1 | 119.8(5) |
| N(1)-Sn(2)-N(2)#1 | 81.2(4) | Ge(1)-N(2)-Sn(1) | 119.2(6) |
| N(1)-Sn(2)-N(1)#1 | 83.0(4) | Sn(1)#1-N(2)-Sn(1) | 98.2(5) |

| | |
|---|---|
| Ge(1)-N(2)-Sn(2)#1 | 120.7(6) |
| Sn(1)#1-N(2)-Sn(2)#1 | 97.2(5) |
| Sn(1)-N(2)-Sn(2)#1 | 96.6(4) |

**Table A.61**. Anisotropic displacement parameters ($Å^2$ x $10^3$) for $C_{12}H_{36}N_4Sn_4Ge_4$ (**16**).

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Sn(1) | 39(1) | 33(1) | 44(1) | 2(1) | 10(1) | 3(1) |
| Sn(2) | 44(1) | 34(1) | 38(1) | -2(1) | 11(1) | -2(1) |
| Ge(1) | 48(1) | 34(1) | 41(1) | -4(1) | 12(1) | 2(1) |
| Ge(2) | 37(1) | 35(1) | 56(1) | 2(1) | 8(1) | -5(1) |
| N(1) | 28(7) | 40(7) | 43(7) | -1(5) | 11(5) | 8(5) |
| N(2) | 38(8) | 29(6) | 48(7) | -4(5) | 7(6) | -9(5) |
| C(1) | 46(11) | 109(17) | 53(11) | 10(10) | 20(9) | 10(11) |
| C(2) | 34(9) | 73(12) | 45(9) | 2(8) | -4(7) | -6(8) |
| C(3) | 91(15) | 42(10) | 74(13) | 14(9) | 23(11) | 10(9) |
| C(4) | 126(18) | 31(8) | 44(9) | -12(7) | 30(10) | -45(10) |
| C(5) | 62(14) | 103(17) | 83(15) | 10(12) | 36(12) | 30(12) |
| C(6) | 67(15) | 94(17) | 85(16) | 26(13) | -19(12) | -16(12) |
| O(1) | 35(6) | 75(8) | 97(9) | -86(7) | 19(6) | -12(5) |

**Table A.62**. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å $^2$ x $10^3$) for $C_{12}H_{36}N_4Sn_4Ge_4$ (**16**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 8009 | 1912 | 4169 | 102 |
| H(1B) | 8577 | 2176 | 5146 | 102 |
| H(1C) | 8637 | 1342 | 4893 | 102 |
| H(2A) | 11301 | 1264 | 5558 | 81 |
| H(2B) | 11485 | 2092 | 5859 | 81 |
| H(2C) | 12041 | 1778 | 5172 | 81 |
| H(3A) | 10901 | 3100 | 3792 | 104 |
| H(3B) | 10299 | 3416 | 4449 | 104 |
| H(3C) | 9609 | 3196 | 3480 | 104 |
| H(4A) | 8999 | -1352 | 2087 | 99 |
| H(4B) | 7855 | -1676 | 1521 | 99 |
| H(4C) | 8147 | -1635 | 2557 | 99 |
| H(5A) | 7372 | -220 | 3403 | 119 |
| H(5B) | 6316 | -624 | 2801 | 119 |
| H(5C) | 6430 | 236 | 2734 | 119 |
| H(6A) | 6179 | 301 | 764 | 137 |
| H(6B) | 6190 | -532 | 491 | 137 |
| H(6C) | 7117 | 7 | 393 | 137 |

**Table A.63**. Atomic Coordinates (x $10^4$) and Equivalent Isotropic Displacement Parameters (Å x $10^3$) for $C_{12}H_{36}N_4Sn_8$ (**17**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Sn(1) | 998(1) | 998(1) | 998(1) | 28(1) |
| Sn(2) | 1903(1) | 1903(1) | -1903(1) | 32(1) |
| N(1) | 887(3) | 887(3) | -887(3) | 29(1) |
| C(1) | 3636(5) | 1461(4) | -1461(4) | 51(1) |

**Table A.64**. Interatomic Distances (Å) and Angles (°) for $C_{12}H_{36}N_4Sn_8$ (**17**).

| | | | |
|---|---|---|---|
| Sn(1)-N(1)#1 | 2.196(3) | Sn(1)#2-Sn(1)-Sn(1)#1 | 60.0 |
| Sn(1)-N(1)#2 | 2.196(3) | N(1)#1-Sn(1)-Sn(1)#3 | 41.76(10) |
| Sn(1)-N(1) | 2.196(3) | N(1)#2-Sn(1)-Sn(1)#3 | 41.76(10) |
| Sn(1)-Sn(1)#2 | 3.2757(9) | N(1)-Sn(1)-Sn(1)#3 | 85.27(15) |
| Sn(1)-Sn(1)#1 | 3.2757(9) | Sn(1)#2-Sn(1)-Sn(1)#3 | 60.0 |
| Sn(1)-Sn(1)#3 | 3.2757(9) | Sn(1)#1-Sn(1)-Sn(1)#3 | 60.0 |
| Sn(2)-N(1) | 2.043(7) | N(1)-Sn(2)-C(1)#4 | 105.43(19) |
| Sn(2)-C(1)#4 | 2.139(5) | N(1)-Sn(2)-C(1) | 105.43(19) |
| Sn(2)-C(1) | 2.139(5) | C(1)#4-Sn(2)-C(1) | 113.20(16) |
| Sn(2)-C(1)#5 | 2.139(5) | N(1)-Sn(2)-C(1)#5 | 105.43(19) |
| N(1)-Sn(1)#1 | 2.196(3) | C(1)#4-Sn(2)-C(1)#5 | 113.20(16) |
| N(1)-Sn(1)#2 | 2.196(3) | C(1)-Sn(2)-C(1)#5 | 113.20(16) |
| N(1)#1-Sn(1)-N(1)#2 | 83.1(2) | Sn(2)-N(1)-Sn(1) | 120.54(15) |
| N(1)#1-Sn(1)-N(1) | 83.1(2) | Sn(2)-N(1)-Sn(1)#1 | 120.54(15) |
| N(1)#2-Sn(1)-N(1) | 83.1(2) | Sn(1)-N(1)-Sn(1)#1 | 96.5(2) |
| N(1)#1-Sn(1)-Sn(1)#2 | 85.27(15) | Sn(2)-N(1)-Sn(1)#2 | 120.54(15) |
| N(1)#2-Sn(1)-Sn(1)#2 | 41.76(10) | Sn(1)-N(1)-Sn(1)#2 | 96.5(2) |
| N(1)-Sn(1)-Sn(1)#2 | 41.76(10) | Sn(1)#1-N(1)-Sn(1)#2 | 96.5(2) |
| N(1)#1-Sn(1)-Sn(1)#1 | 41.76(10) | | |
| N(1)#2-Sn(1)-Sn(1)#1 | 85.27(15) | | |
| N(1)-Sn(1)-Sn(1)#1 | 41.76(10) | | |

**Table A.65**. Anisotropic displacement parameters ($Å^2$ x $10^3$) for $C_{12}H_{36}N_4Sn_8$ (**17**).

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Sn(1) | 28(1) | 28(1) | 28(1) | -3(1) | -3(1) | -3(1) |
| Sn(2) | 32(1) | 32(1) | 32(1) | 5(1) | 5(1) | -5(1) |
| N(1) | 29(1) | 29(1) | 29(1) | 1(1) | 1(1) | -1(1) |
| C(1) | 34(2) | 59(2) | 59(2) | 6(3) | 4(2) | -4(2) |

**Table A.66**. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å $^2$ x $10^3$) for $C_{12}H_{36}N_4Sn_8$ (**17**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 3677 | 1277 | -656 | 42(16) |
| H(1B) | 4134 | 2101 | -1623 | 42(16) |
| H(1C) | 3875 | 806 | -1906 | 42(16) |

**Table A.67**. Atomic Coordinates (x $10^4$) and Equivalent Isotropic Displacement Parameters (Å x $10^3$) for $C_{12}H_{36}N_4Ge_8$ (**18**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Ge(1) | 4070(1) | 4070(1) | 4070(1) | 26(1) |
| Ge(2) | 1796(1) | 1796(1) | 1796(1) | 31(1) |
| N(1) | 839(4) | 839(4) | 839(4) | 27(2) |
| C(1) | 3422(6) | 1407(5) | 1407(5) | 49(2) |

**Table A.68** Interatomic Distances (Å) and Angles (°) for $C_{12}H_{36}N_4Ge_8$ (**18**).

| | | | |
|---|---|---|---|
| Ge(1)-N(1)#1 | 2.002(4) | N(1)-Ge(2)-C(1) | 106.6(2) |
| Ge(1)-N(1)#2 | 2.002(4) | N(1)-Ge(2)-C(1)#4 | 106.6(2) |
| Ge(1)-N(1)#3 | 2.002(4) | C(1)-Ge(2)-C(1)#4 | 112.2(2) |
| Ge(2)-N(1) | 1.870(9) | N(1)-Ge(2)-C(1)#5 | 106.6(2) |
| Ge(2)-C(1) | 1.937(7) | C(1)-Ge(2)-C(1)#5 | 112.2(2) |
| Ge(2)-C(1)#4 | 1.937(7) | C(1)#4-Ge(2)-C(1)#5 | 112.2(2) |
| Ge(2)-C(1)#5 | 1.937(7) | Ge(2)-N(1)-Ge(1)#6 | 121.1(2) |
| N(1)-Ge(1)#6 | 2.002(4) | Ge(2)-N(1)-Ge(1)#7 | 121.1(2) |
| N(1)-Ge(1)#7 | 2.002(4) | Ge(1)#6-N(1)-Ge(1)#7 | 95.7(3) |
| N(1)-Ge(1)#8 | 2.002(4) | Ge(2)-N(1)-Ge(1)#8 | 121.1(2) |
| N(1)#1-Ge(1)-N(1)#2 | 84.0(3) | Ge(1)#6-N(1)-Ge(1)#8 | 95.7(3) |
| N(1)#1-Ge(1)-N(1)#3 | 84.0(3) | Ge(1)#7-N(1)-Ge(1)#8 | 95.7(3) |
| N(1)#2-Ge(1)-N(1)#3 | 84.0(3) | | |

**Table A.69**. Anisotropic displacement parameters ($Å^2$ x $10^3$) for $C_{12}H_{36}N_4Ge_8$ (**18**).

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Ge(1) | 26(1) | 26(1) | 26(1) | -2(1) | -2(1) | -2(1) |
| Ge(2) | 31(1) | 31(1) | 31(1) | -5(1) | -5(1) | -5(1) |
| N(1) | 27(2) | 27(2) | 27(2) | -1(2) | -1(2) | -1(2) |
| C(1) | 29(4) | 59(3) | 59(3) | 0(4) | -6(3) | -6(3) |

**Table A.70**. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å $^2$ x $10^3$) for $C_{12}H_{36}N_4Ge_8$ (**18**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 3524 | 571 | 1431 | 80(20) |
| H(1B) | 3938 | 1769 | 1964 | 80(20) |
| H(1C) | 3600 | 1689 | 634 | 80(20) |

**Table A.71**. Atomic Coordinates (x $10^4$) and Equivalent Isotropic Displacement Parameters (Å x $10^3$) for $C_{12}H_{36}N_4Pb_4Ge_4$ (**19**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Pb(1) | -673(1) | -673(1) | -10673(1) | 36(1) |
| Pb(2) | -674(1) | -1823(1) | -5666(1) | 34(1) |
| Ge(1) | -1163(2) | -1163(2) | -8838(2) | 50(2) |
| Ge(2) | 1179(2) | -1378(2) | -6189(2) | 45(1) |
| N(1) | -585(9) | -585(9) | -9415(9) | 48(9) |
| N(2) | 552(8) | -1928(9) | -5581(8) | 30(3) |
| C(1) | -1172(15) | -862(17) | -7802(16) | 102(13) |
| C(2) | 1730(60) | -2130(60) | -7140(60) | 50(30) |
| C(2A) | 1031(19) | -1683(19) | -7198(19) | 64(9) |
| C(3) | 2128(18) | -1867(19) | -6204(17) | 63(10) |
| C(3A) | 1780(90) | -2630(90) | -6520(90) | 90(50) |
| C(4) | 1230(30) | -360(30) | -5880(30) | 48(12) |
| C(4A) | 770(30) | -340(30) | -6190(20) | 51(12) |

**Table A.72**. Interatomic Distances (Å) and Angles (°) for $C_{12}H_{36}N_4Pb_4Ge_4$ (**19**).

| | | | |
|---|---|---|---|
| Pb(1)-N(1) | 2.303(14) | Ge(2)-C(2) | 2.42(10) |
| Pb(1)-N(1)#1 | 2.303(14) | N(1)-Pb(1)#1 | 2.303(14) |
| Pb(1)-N(1)#2 | 2.303(14) | N(1)-Pb(1)#2 | 2.303(14) |
| Pb(1)-Pb(1)#1 | 3.467(2) | N(2)-Pb(2)#4 | 2.291(15) |
| Pb(1)-Pb(1)#2 | 3.467(2) | N(2)-Pb(2)#6 | 2.293(16) |
| Pb(1)-Pb(1)#3 | 3.467(2) | C(2)-C(3A) | 1.46(16) |
| Pb(2)-N(2) | 2.247(15) | C(2)-C(2A) | 1.51(10) |
| Pb(2)-N(2)#4 | 2.291(15) | C(2)-C(3) | 1.91(12) |
| Pb(2)-N(2)#5 | 2.293(16) | C(3)-C(3A) | 1.64(16) |
| Pb(2)-C(3A)#5 | 2.73(15) | C(3A)-Pb(2)#6 | 2.73(15) |
| Pb(2)-Pb(2)#4 | 3.4525(15) | C(4)-C(4A) | 1.03(6) |
| Pb(2)-Pb(2)#6 | 3.4718(13) | N(1)-Pb(1)-N(1)#1 | 81.8(9) |
| Pb(2)-Pb(2)#5 | 3.4718(13) | N(1)-Pb(1)-N(1)#2 | 81.8(9) |
| Ge(1)-N(1) | 1.82(3) | N(1)#1-Pb(1)-N(1)#2 | 81.8(9) |
| Ge(1)-C(1)#7 | 1.96(3) | N(1)-Pb(1)-Pb(1)#1 | 41.2(4) |
| Ge(1)-C(1)#8 | 1.96(3) | N(1)#1-Pb(1)-Pb(1)#1 | 41.2(4) |
| Ge(1)-C(1) | 1.96(3) | N(1)#2-Pb(1)-Pb(1)#1 | 84.4(6) |
| Ge(2)-N(2) | 1.882(19) | N(1)-Pb(1)-Pb(1)#2 | 41.2(4) |
| Ge(2)-C(2A) | 1.94(3) | N(1)#1-Pb(1)-Pb(1)#2 | 84.4(6) |
| Ge(2)-C(4) | 1.95(5) | N(1)#2-Pb(1)-Pb(1)#2 | 41.2(4) |
| Ge(2)-C(3) | 1.95(3) | Pb(1)#1-Pb(1)-Pb(1)#2 | 60.0 |
| Ge(2)-C(4A) | 2.04(5) | N(1)-Pb(1)-Pb(1)#3 | 84.4(6) |

| | | | |
|---|---|---|---|
| N(1)#1-Pb(1)-Pb(1)#3 | 41.2(4) | Pb(2)#4-Pb(2)-Pb(2)#5 | 60.184(12) |
| N(1)#2-Pb(1)-Pb(1)#3 | 41.2(4) | Pb(2)#6-Pb(2)-Pb(2)#5 | 59.63(2) |
| Pb(1)#1-Pb(1)-Pb(1)#3 | 60.0 | N(1)-Ge(1)-C(1)#7 | 113.5(9) |
| Pb(1)#2-Pb(1)-Pb(1)#3 | 60.0 | N(1)-Ge(1)-C(1)#8 | 113.5(9) |
| N(2)-Pb(2)-N(2)#4 | 80.1(7) | C(1)#7-Ge(1)-C(1)#8 | 105.2(10) |
| N(2)-Pb(2)-N(2)#5 | 80.5(7) | N(1)-Ge(1)-C(1) | 113.5(9) |
| N(2)#4-Pb(2)-N(2)#5 | 79.6(7) | C(1)#7-Ge(1)-C(1) | 105.2(10) |
| N(2)-Pb(2)-C(3A)#5 | 125(3) | C(1)#8-Ge(1)-C(1) | 105.2(10) |
| N(2)#4-Pb(2)-C(3A)#5 | 140(3) | N(2)-Ge(2)-C(2A) | 108.7(12) |
| N(2)#5-Pb(2)-C(3A)#5 | 75(3) | N(2)-Ge(2)-C(4) | 111.6(16) |
| N(2)-Pb(2)-Pb(2)#4 | 40.9(4) | C(2A)-Ge(2)-C(4) | 123.9(18) |
| N(2)#4-Pb(2)-Pb(2)#4 | 40.0(4) | N(2)-Ge(2)-C(3) | 107.7(10) |
| N(2)#5-Pb(2)-Pb(2)#4 | 83.3(4) | C(2A)-Ge(2)-C(3) | 88.7(13) |
| C(3A)#5-Pb(2)-Pb(2)#4 | 157(3) | C(4)-Ge(2)-C(3) | 113.4(18) |
| N(2)-Pb(2)-Pb(2)#6 | 40.6(4) | N(2)-Ge(2)-C(4A) | 106.0(14) |
| N(2)#4-Pb(2)-Pb(2)#6 | 82.9(5) | C(2A)-Ge(2)-C(4A) | 102.3(15) |
| N(2)#5-Pb(2)-Pb(2)#6 | 40.7(4) | C(4)-Ge(2)-C(4A) | 29.7(17) |
| C(3A)#5-Pb(2)-Pb(2)#6 | 98(3) | C(3)-Ge(2)-C(4A) | 138.8(19) |
| Pb(2)#4-Pb(2)-Pb(2)#6 | 60.184(12) | N(2)-Ge(2)-C(2) | 112(3) |
| N(2)-Pb(2)-Pb(2)#5 | 83.5(5) | C(2A)-Ge(2)-C(2) | 39(3) |
| N(2)#4-Pb(2)-Pb(2)#5 | 40.8(4) | C(4)-Ge(2)-C(2) | 137(3) |
| N(2)#5-Pb(2)-Pb(2)#5 | 39.6(4) | C(3)-Ge(2)-C(2) | 50(3) |
| C(3A)#5-Pb(2)-Pb(2)#5 | 105(3) | C(4A)-Ge(2)-C(2) | 132(3) |

| | | | |
|---|---|---|---|
| Ge(1)-N(1)-Pb(1) | 119.6(6) | C(2A)-C(2)-Ge(2) | 53(3) |
| Ge(1)-N(1)-Pb(1)#1 | 119.6(6) | C(3)-C(2)-Ge(2) | 52(3) |
| Pb(1)-N(1)-Pb(1)#1 | 97.7(8) | C(2)-C(2A)-Ge(2) | 88(5) |
| Ge(1)-N(1)-Pb(1)#2 | 119.6(6) | C(3A)-C(3)-C(2) | 48(6) |
| Pb(1)-N(1)-Pb(1)#2 | 97.7(8) | C(3A)-C(3)-Ge(2) | 93(6) |
| Pb(1)#1-N(1)-Pb(1)#2 | 97.7(8) | C(2)-C(3)-Ge(2) | 78(3) |
| Ge(2)-N(2)-Pb(2) | 121.2(7) | C(2)-C(3A)-C(3) | 76(8) |
| Ge(2)-N(2)-Pb(2)#4 | 118.7(8) | C(2)-C(3A)-Pb(2)#6 | 128(10) |
| Pb(2)-N(2)-Pb(2)#4 | 99.1(6) | C(3)-C(3A)-Pb(2)#6 | 114(8) |
| Ge(2)-N(2)-Pb(2)#6 | 115.5(7) | C(4A)-C(4)-Ge(2) | 80(5) |
| Pb(2)-N(2)-Pb(2)#6 | 99.8(7) | C(4)-C(4A)-Ge(2) | 70(4) |
| Pb(2)#4-N(2)-Pb(2)#6 | 98.5(6) | | |
| C(3A)-C(2)-C(2A) | 117(10) | | |
| C(3A)-C(2)-C(3) | 56(8) | | |
| C(2A)-C(2)-C(3) | 105(6) | | |
| C(3A)-C(2)-Ge(2) | 80(8) | | |

**Table A.73**. Anisotropic displacement parameters ($Å^2$ x $10^3$) for $C_{12}H_{36}N_4Pb_4Ge_4$ (**19**).

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Pb(1) | 36(1) | 36(1) | 36(1) | -4(1) | -4(1) | -4(1) |
| Pb(2) | 35(1) | 30(1) | 36(1) | 3(1) | -6(1) | 3(1) |
| Ge(1) | 50(2) | 50(2) | 50(2) | 10(1) | 10(1) | -10(1) |
| Ge(2) | 45(1) | 44(1) | 45(2) | 17(2) | 6(1) | -12(1) |
| N(1) | 48(9) | 48(9) | 48(9) | 9(9) | 9(9) | -9(9) |
| N(2) | 29(8) | 29(8) | 32(9) | -6(7) | -11(7) | 13(6) |
| C(1) | 80(20) | 140(30) | 90(30) | 60(20) | 29(18) | 0(20) |

**Table A.74**. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å $^2$ x $10^3$) for $C_{12}H_{36}N_4Pb_4Ge_4$ (**19**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | -1324 | -1263 | -7506 | 153 |
| H(1B) | -1504 | -465 | -7740 | 153 |
| H(1C) | -693 | -712 | -7661 | 153 |

**Table A.75**. Atomic Coordinates (x $10^4$) and Equivalent Isotropic Displacement Parameters (Å x $10^3$) for $C_{12}H_{28}O_8Sn_6$ (**21**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Sn(1) | 9299(1) | 439(1) | 3991(1) | 34(1) |
| Sn(2) | 9275(1) | 2500 | 5694(1) | 30(1) |
| Sn(3) | 12070(1) | 1435(1) | 5139(1) | 32(1) |
| Sn(4) | 12103(1) | 2500 | 3438(1) | 31(1) |
| O(1) | 8063(9) | 2500 | 4572(6) | 33(3) |
| O(2) | 11549(11) | 2500 | 6003(6) | 33(3) |
| O(3) | 11595(8) | 1167(5) | 3854(4) | 32(2) |
| O(4) | 10084(7) | 1571(4) | 5046(4) | 23(2) |
| O(5) | 12500(11) | 2500 | 4576(5) | 28(2) |
| O(6) | 10093(10) | 2500 | 3580(5) | 25(2) |
| C(1) | 6634(15) | 2500 | 4589(10) | 36(4) |
| C(2) | 6160(20) | 2500 | 3804(11) | 55(6) |
| C(3) | 6193(14) | 1743(11) | 4980(9) | 58(4) |
| C(4) | 11996(14) | 2500 | 6753(10) | 37(4) |
| C(5) | 13500(20) | 2500 | 6772(12) | 83(9) |
| C(6) | 11532(15) | 1759(10) | 7153(8) | 57(4) |
| C(7) | 12051(10) | 447(8) | 3484(7) | 33(3) |
| C(8) | 11628(17) | 476(10) | 2683(7) | 59(4) |
| C(9) | 13503(14) | 437(10) | 3534(9) | 59(4) |
| C(10) | 11519(18) | -289(9) | 3852(8) | 58(4) |

**Table A.76**. Interatomic Distances (Å) and Angles (°) for $C_{12}H_{28}O_8Sn_6$ (**21**).

| | | | |
|---|---|---|---|
| Sn(1)-O(4) | 2.064(7) | O(6)-Sn(1)#1 | 2.065(5) |
| Sn(1)-O(6) | 2.065(5) | C(1)-C(2) | 1.48(3) |
| Sn(1)-O(1) | 2.400(7) | C(1)-C(3) | 1.501(18) |
| Sn(1)-O(3) | 2.418(8) | C(1)-C(3)#1 | 1.501(18) |
| Sn(2)-O(4) | 2.092(7) | C(4)-C(6) | 1.493(18) |
| Sn(2)-O(4)#1 | 2.092(7) | C(4)-C(6)#1 | 1.493(18) |
| Sn(2)-O(1) | 2.361(11) | C(4)-C(5) | 1.55(2) |
| Sn(2)-O(2) | 2.406(11) | C(7)-C(10) | 1.484(18) |
| Sn(3)-O(4) | 2.064(7) | C(7)-C(8) | 1.498(18) |
| Sn(3)-O(5) | 2.071(5) | C(7)-C(9) | 1.498(18) |
| Sn(3)-O(3) | 2.389(8) | O(4)-Sn(1)-O(6) | 94.6(3) |
| Sn(3)-O(2) | 2.399(8) | O(4)-Sn(1)-O(1) | 74.6(3) |
| Sn(4)-O(5) | 2.074(10) | O(6)-Sn(1)-O(1) | 75.3(3) |
| Sn(4)-O(6) | 2.085(10) | O(4)-Sn(1)-O(3) | 74.3(3) |
| Sn(4)-O(3) | 2.379(9) | O(6)-Sn(1)-O(3) | 74.6(3) |
| Sn(4)-O(3)#1 | 2.379(9) | O(1)-Sn(1)-O(3) | 134.2(3) |
| O(1)-C(1) | 1.471(18) | O(4)-Sn(2)-O(4)#1 | 94.1(4) |
| O(1)-Sn(1)#1 | 2.400(7) | O(4)-Sn(2)-O(1) | 75.0(3) |
| O(2)-C(4) | 1.42(2) | O(4)#1-Sn(2)-O(1) | 75.0(3) |
| O(2)-Sn(3)#1 | 2.399(8) | O(4)-Sn(2)-O(2) | 74.9(3) |
| O(3)-C(7) | 1.437(15) | O(4)#1-Sn(2)-O(2) | 74.9(3) |
| O(5)-Sn(3)#1 | 2.071(5) | O(1)-Sn(2)-O(2) | 135.2(4) |

| | | | |
|---|---|---|---|
| O(4)-Sn(3)-O(5) | 94.6(4) | Sn(3)#1-O(2)-Sn(2) | 94.0(3) |
| O(4)-Sn(3)-O(3) | 74.9(3) | C(7)-O(3)-Sn(4) | 123.1(6) |
| O(5)-Sn(3)-O(3) | 74.6(3) | C(7)-O(3)-Sn(3) | 121.9(7) |
| O(4)-Sn(3)-O(2) | 75.6(3) | Sn(4)-O(3)-Sn(3) | 94.8(3) |
| O(5)-Sn(3)-O(2) | 75.0(3) | C(7)-O(3)-Sn(1) | 121.3(6) |
| O(3)-Sn(3)-O(2) | 135.1(3) | Sn(4)-O(3)-Sn(1) | 94.3(3) |
| O(5)-Sn(4)-O(6) | 94.4(4) | Sn(3)-O(3)-Sn(1) | 94.0(3) |
| O(5)-Sn(4)-O(3) | 74.7(2) | Sn(1)-O(4)-Sn(3) | 116.7(3) |
| O(6)-Sn(4)-O(3) | 75.1(2) | Sn(1)-O(4)-Sn(2) | 115.3(3) |
| O(5)-Sn(4)-O(3)#1 | 74.7(2) | Sn(3)-O(4)-Sn(2) | 115.4(3) |
| O(6)-Sn(4)-O(3)#1 | 75.1(2) | Sn(3)-O(5)-Sn(3)#1 | 115.9(5) |
| O(3)-Sn(4)-O(3)#1 | 135.0(4) | Sn(3)-O(5)-Sn(4) | 115.7(3) |
| C(1)-O(1)-Sn(2) | 120.8(10) | Sn(3)#1-O(5)-Sn(4) | 115.7(3) |
| C(1)-O(1)-Sn(1) | 122.6(5) | Sn(1)-O(6)-Sn(1)#1 | 115.7(5) |
| Sn(2)-O(1)-Sn(1) | 95.0(3) | Sn(1)-O(6)-Sn(4) | 115.9(3) |
| C(1)-O(1)-Sn(1)#1 | 122.6(5) | Sn(1)#1-O(6)-Sn(4) | 115.9(3) |
| Sn(2)-O(1)-Sn(1)#1 | 95.0(3) | O(1)-C(1)-C(2) | 107.9(14) |
| Sn(1)-O(1)-Sn(1)#1 | 93.5(4) | O(1)-C(1)-C(3) | 108.2(10) |
| C(4)-O(2)-Sn(3) | 122.4(5) | C(2)-C(1)-C(3) | 110.0(10) |
| C(4)-O(2)-Sn(3)#1 | 122.4(5) | O(1)-C(1)-C(3)#1 | 108.2(10) |
| Sn(3)-O(2)-Sn(3)#1 | 94.1(4) | C(2)-C(1)-C(3)#1 | 110.0(10) |
| C(4)-O(2)-Sn(2) | 122.2(9) | C(3)-C(1)-C(3)#1 | 112.5(18) |
| Sn(3)-O(2)-Sn(2) | 94.0(3) | O(2)-C(4)-C(6) | 110.4(10) |

| | | | |
|---|---|---|---|
| O(2)-C(4)-C(6)#1 | 110.4(9) | O(3)-C(7)-C(8) | 108.6(10) |
| C(6)-C(4)-C(6)#1 | 109.8(16) | C(10)-C(7)-C(8) | 110.0(13) |
| O(2)-C(4)-C(5) | 110.1(14) | O(3)-C(7)-C(9) | 108.0(10) |
| C(6)-C(4)-C(5) | 108.0(10) | C(10)-C(7)-C(9) | 109.4(13) |
| C(6)#1-C(4)-C(5) | 108.0(10) | C(8)-C(7)-C(9) | 110.3(12) |
| O(3)-C(7)-C(10) | 110.5(10) | | |

**Table A.77**. Anisotropic displacement parameters ($Å^2$ x $10^3$) for $C_{12}H_{28}O_8Sn_6$ (**21**).

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Sn(1) | 34(1) | 40(1) | 29(1) | -2(1) | -2(1) | -12(1) |
| Sn(2) | 28(1) | 36(1) | 25(1) | 0 | 8(1) | 0 |
| Sn(3) | 26(1) | 37(1) | 33(1) | 7(1) | 2(1) | 4(1) |
| Sn(4) | 27(1) | 40(1) | 25(1) | 0 | 5(1) | 0 |
| O(1) | 18(5) | 51(8) | 29(6) | 0 | -2(4) | 0 |
| O(2) | 31(6) | 47(8) | 22(6) | 0 | -7(5) | 0 |
| O(3) | 36(4) | 34(5) | 26(4) | -6(3) | 10(3) | -3(4) |
| O(4) | 19(3) | 23(4) | 28(4) | -1(3) | 2(3) | -2(3) |
| O(5) | 41(6) | 29(7) | 14(5) | 0 | -1(5) | 0 |
| O(6) | 23(5) | 38(7) | 15(5) | 0 | -3(4) | 0 |
| C(1) | 17(7) | 47(12) | 44(10) | 0 | 0(7) | 0 |
| C(2) | 38(10) | 81(17) | 48(12) | 0 | -7(9) | 0 |
| C(3) | 33(7) | 69(12) | 73(11) | 15(9) | 1(7) | -13(7) |
| C(4) | 15(7) | 53(13) | 43(10) | 0 | -6(7) | 0 |
| C(5) | 40(11) | 180(30) | 29(11) | 0 | -10(9) | 0 |
| C(6) | 75(10) | 66(11) | 30(7) | 6(7) | 7(7) | 22(9) |
| C(7) | 20(5) | 32(8) | 48(7) | 4(6) | 10(5) | -2(5) |
| C(8) | 100(13) | 49(10) | 26(7) | -12(6) | 13(7) | 15(9) |
| C(9) | 54(9) | 58(11) | 65(10) | -24(8) | 24(8) | -5(8) |
| C(10) | 92(12) | 29(9) | 53(9) | 1(6) | 21(9) | -5(8) |

**Table A.78**. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å $^2$ x $10^3$) for $C_{12}H_{28}O_8Sn_6$ (**21**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2A) | 5243 | 2463 | 3800 | 80 |
| H(2B) | 6521 | 2049 | 3546 | 80 |
| H(2C) | 6425 | 2988 | 3565 | 80 |
| H(3A) | 6368 | 1286 | 4673 | 80(30) |
| H(3B) | 5287 | 1775 | 5075 | 80(30) |
| H(3C) | 6646 | 1688 | 5441 | 80(30) |
| H(5A) | 13809 | 1964 | 6692 | 80 |
| H(5B) | 13789 | 2689 | 7245 | 80 |
| H(5C) | 13820 | 2846 | 6389 | 80 |
| H(6A) | 10610 | 1749 | 7153 | 34(19) |
| H(6B) | 11840 | 1767 | 7654 | 34(19) |
| H(6C) | 11853 | 1290 | 6906 | 34(19) |
| H(8A) | 10707 | 495 | 2659 | 110(40) |
| H(8B) | 11930 | 6 | 2430 | 110(40) |
| H(8C) | 11978 | 946 | 2451 | 110(40) |
| H(9A) | 13843 | 917 | 3316 | 60(30) |
| H(9B) | 13830 | -22 | 3273 | 60(30) |
| H(9C) | 13758 | 408 | 4044 | 60(30) |
| H(10A) | 11863 | -332 | 4343 | 60(30) |
| H(10B) | 11754 | -755 | 3570 | 60(30) |
| H(10C) | 10599 | -250 | 3877 | 60(30) |

**Table A.79**. Atomic Coordinates (x $10^4$) and Equivalent Isotropic Displacement Parameters (Å x $10^3$) for $C_{16}H_{36}O_8Sn_6$ (**22**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Sn(1) | 0 | 7500 | 125(1) | 23(1) |
| Sn(2) | -1975(1) | 6633(1) | -1259(1) | 23(1) |
| O(1) | 1776(3) | 6842(3) | -382(2) | 24(1) |
| O(2) | -479(2) | 6254(2) | -655(1) | 16(1) |
| C(1) | -2636(4) | 8516(4) | 132(2) | 25(1) |
| C(2) | -3052(4) | 7497(4) | 589(3) | 36(1) |
| C(3) | -3635(4) | 9085(4) | -268(3) | 39(1) |

**Table A.80**. Interatomic Distances (Å) and Angles (°) for $C_{16}H_{36}O_8Sn_6$ (**22**).

| | | | |
|---|---|---|---|
| Sn(1)-O(2) | 2.091(3) | O(2)#2-Sn(2)-O(1)#1 | 74.84(10) |
| Sn(1)-O(2)#1 | 2.091(3) | O(2)-Sn(2)-O(1)#1 | 74.40(10) |
| Sn(1)-O(1) | 2.379(3) | O(2)#2-Sn(2)-O(1)#2 | 75.11(10) |
| Sn(1)-O(1)#1 | 2.379(3) | O(2)-Sn(2)-O(1)#2 | 73.59(10) |
| Sn(2)-O(2)#2 | 2.067(3) | O(1)#1-Sn(2)-O(1)#2 | 133.41(13) |
| Sn(2)-O(2) | 2.095(3) | C(1)#1-O(1)-Sn(1) | 116.9(2) |
| Sn(2)-O(1)#1 | 2.383(3) | C(1)#1-O(1)-Sn(2)#1 | 125.4(3) |
| Sn(2)-O(1)#2 | 2.418(3) | Sn(1)-O(1)-Sn(2)#1 | 95.74(11) |
| O(1)-C(1)#1 | 1.423(5) | C(1)#1-O(1)-Sn(2)#3 | 122.5(2) |
| O(1)-Sn(2)#1 | 2.383(3) | Sn(1)-O(1)-Sn(2)#3 | 94.05(10) |
| O(1)-Sn(2)#3 | 2.418(3) | Sn(2)#1-O(1)-Sn(2)#3 | 94.97(10) |
| O(2)-Sn(2)#3 | 2.067(3) | Sn(2)#3-O(2)-Sn(1) | 115.21(12) |
| C(1)-O(1)#1 | 1.423(5) | Sn(2)#3-O(2)-Sn(2) | 116.51(12) |
| C(1)-C(3) | 1.516(7) | Sn(1)-O(2)-Sn(2) | 115.09(12) |
| C(1)-C(2) | 1.520(6) | O(1)#1-C(1)-C(3) | 110.8(4) |
| O(2)-Sn(1)-O(2)#1 | 95.57(14) | O(1)#1-C(1)-C(2) | 110.3(4) |
| O(2)-Sn(1)-O(1) | 75.57(10) | C(3)-C(1)-C(2) | 110.7(4) |
| O(2)#1-Sn(1)-O(1) | 74.57(10) | | |
| O(2)-Sn(1)-O(1)#1 | 74.57(10) | | |
| O(2)#1-Sn(1)-O(1)#1 | 75.57(10) | | |
| O(1)-Sn(1)-O(1)#1 | 134.91(14) | | |
| O(2)#2-Sn(2)-O(2) | 94.85(14) | | |

**Table A.81**. Anisotropic displacement parameters ($Å^2$ x $10^3$) for $C_{16}H_{36}O_8Sn_6$ (**22**).

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Sn(1) | 26(1) | 22(1) | 20(1) | 0 | 0 | -2(1) |
| Sn(2) | 17(1) | 22(1) | 30(1) | 3(1) | -1(1) | -3(1) |
| O(1) | 20(2) | 26(2) | 26(2) | 0(1) | -5(1) | 3(1) |
| O(2) | 14(1) | 16(1) | 18(1) | -1(1) | 0(1) | -3(1) |
| C(1) | 26(3) | 23(2) | 25(2) | -4(2) | 5(2) | 3(2) |
| C(2) | 31(3) | 36(3) | 41(3) | 6(2) | 15(2) | 2(2) |
| C(3) | 38(3) | 38(3) | 40(3) | 6(2) | 13(2) | 14(3) |

**Table A.82**. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å $^2$ x $10^3$) for $C_{16}H_{36}O_8Sn_6$ (**22**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | -2303 | 9065 | 459 | 46(16) |
| H(2A) | -3360 | 6925 | 268 | 49(10) |
| H(2B) | -3632 | 7745 | 924 | 49(10) |
| H(2C) | -2424 | 7182 | 859 | 49(10) |
| H(3A) | -3360 | 9721 | -548 | 45(9) |
| H(3B) | -4183 | 9348 | 86 | 45(9) |
| H(3C) | -3989 | 8544 | -591 | 45(9) |